



## Review

## Modified metal-organic frameworks as photocatalysts

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## ABSTRACT

Photocatalysis is a promising and ideal technology to utilize solar energy for energy regeneration and environmental remediation. Photocatalysis based on metal-organic frameworks (MOFs) has attracted extensive attention because of their excellent properties such as tunable structure and optical properties. This review principally summarizes the progress of various modification strategies, including decoration of organic linker or metal center, combination with semiconductors and metal nanoparticles loading, applied to different MOFs (mainly UiOs, MILs, and ZIFs), and their specific applications were summarized as well. In addition, the existing problems and the development prospect of MOFs for photocatalysis were also presented.

## 1. Introduction

Photocatalysis is a convenient and environmental-friendly approach to convert solar energy into chemical energy. Great progress has been made since the pioneering work on solar energy conversion using TiO<sub>2</sub> photocatalysts reported by Fujishima and Honda in 1972 [1]. From nature photosynthesis to artificial employment of the solar energy, photocatalysis plays an increasingly important role in many fields, such as clean chemicals synthesis, environmental remediation (e.g. degradation of organic dyes [2,3], reduction of heavy metal ions in wastewater [4], and inhibition of air pollutants [5]) energy regeneration (e.g. splitting of water into H<sub>2</sub> [6,7], and CO<sub>2</sub> photocatalytic reduction into solar fuels [8,9]). Researchers have already developed numerous materials as the photocatalysts, and the earliest study is based on the TiO<sub>2</sub> semiconductor material [10,11] and its modification [12,13]. Meanwhile, some novel photocatalytic semiconductors have emerged, such as g-C<sub>3</sub>N<sub>4</sub> [14–16], ZnO [17,18], Ag<sub>3</sub>PO<sub>4</sub> [19,20] and their composites [21,22]. However, the large band gap and the ready recombination of electron-hole pairs lead to low photocatalytic efficiency and poor practicality; moreover, the non-adjustable structure of conventional semiconductor materials limited their further

development in the field of photocatalysis. Therefore, it is highly imperative to explore efficient, robust and cost-effective photocatalytic materials to replace the traditional ones.

Owing to the large surface areas, well-ordered porous structures and tunable organic linkers or metal clusters, the newly emerged functional inorganic-organic hybrid materials of metal-organic frameworks (MOFs) [23,24] have attracted considerable interest in numerous fields, such as gas storage [25,26], separation [27–29], drug delivery [30], chemical sensors [31] and heterogeneous catalysis [32–35]. Among heterogeneous catalysis, utilizing MOFs for photocatalysis is a very significant work in the future [36,37], which is mainly based on two aspects: (1) Pristine MOFs as photocatalysts. These porous materials can act as catalysts themselves not only because the above-mentioned physical merits but also the chemical advantages (existence of open metal sites, unsaturated metal centers and even the catalytically active organic linkers [38]). In addition, some MOFs can act as semiconductors (e.g. MOF-5 [39], NTU-9 [40] and UiO-66 [41–43]), wherein the energy transfer takes place from the organic linker to the metal-oxo cluster. However, most MOFs as photocatalysts possess a large band gap that can merely harvest UV light, which immensely limits their further application. (2) Modified MOFs as photocatalysts.

**Abbreviations:** MOF, metal-organic framework; UiO, University of Oslo; MIL, Materials of Institut Lavoisier; ZIF, zeolitic imidazolate framework; VB, valence band; CB, conduction band; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; UV, ultraviolet; UV-vis, ultraviolet-visible; OG, orange G; RhB, rhodamine B; RBBR, Remazol Brilliant Blue R; MB, methylene blue; MO, methyl orange; ErB, Erythrosin B; Rh6G, rhodamine 6G; DRS, diffuse reflective spectra; DOS, density of states; LMCT, ligand-to-metal charge transfer; BDC, terephthalic acid; MNP, metal nanoparticle; GR, graphene; RGO, reduced graphene oxide; SBU, secondary building units; PC, pyridinecarboxaldehyde; PSE, post-synthetic exchange; DFT, density functional theory; ESR, electron spin resonance; ATA, 2-aminoterephthalic acid; CNNS, carbon nitride nanosheet; PANI, polyaniline; SPR, surface plasmon resonance; PCVG, photochemical vapor generation; PHIK, heptazine imide; AC, acetylacetone; CoIIIBr<sub>2</sub>(LH), co-dioxime-diimine; MOCVD, metal-organic chemical vapor deposition; POM, polyoxometalate; PPCP, pharmaceutical and personal care product; MAG-MIL, magnetic MIL-53(Fe); TEOA, triethanolamine; NC, nanocube; PEC, photoelectrochemical; OER, oxygen evolution reaction; BP, black phosphorus; PMS, peroxymonosulfate; TEM, transmission electron microscope; SEM, scanning electron microscope

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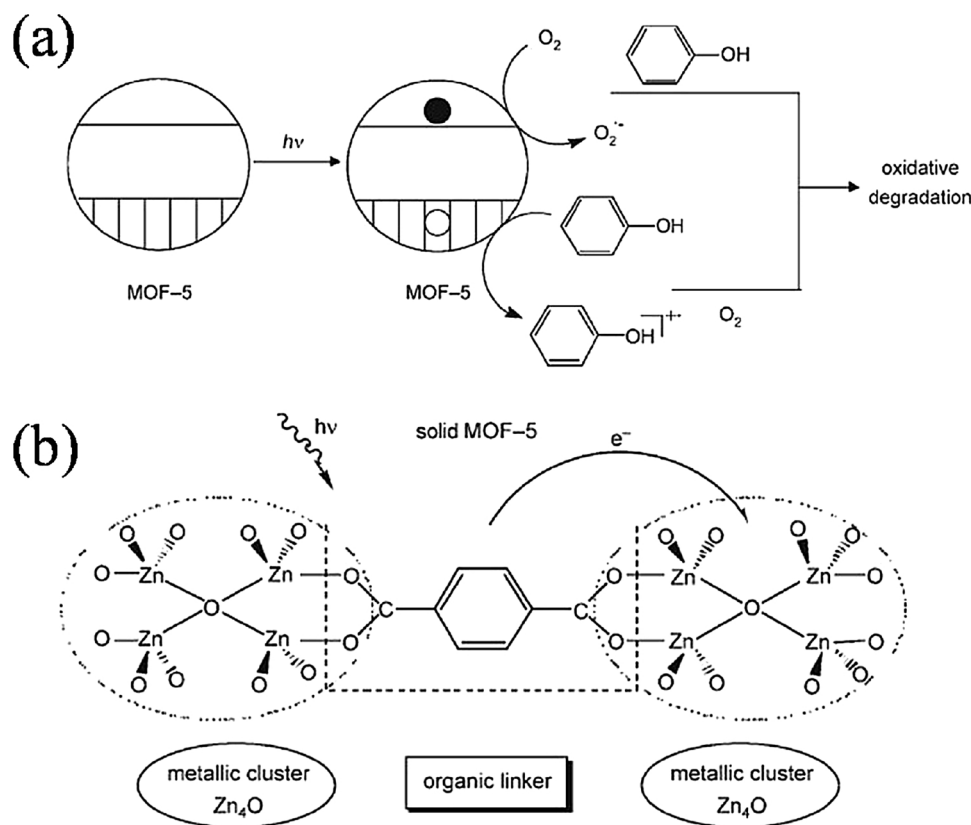


Fig. 1. The possible mechanism of oxidative photocatalytic degradation by MOF-5 (a) and photophysical processes that occur after the irradiation of the MOF-5 solid material (b) [52].

There are several different strategies, including decoration of linker or metal center [44,45], combination with semiconductors [41,46] and sensitization by such as dyes [42,43]. This way is particularly important because it extensively functionalizes MOFs for visible light-induced photocatalysis, thereby leading to a far-reaching development of MOFs as photocatalysts.

Therefore, this review mainly concentrates on the state-of-the-art advance of MOFs-based photocatalysts, covering the representative MOFs such as UiOs, MILs and ZIFs, modification strategies, and their applications. Finally, the existing problems of the existent MOFs photocatalysts are pointed out and the future perspectives are proposed.

## 2. Pristine MOFs

A semiconductor photocatalyst has its band gap. When the energy provided by light illumination is higher than the band gap energy, the negative electrons ( $e^-$ ) in the valance band (VB) will move to the conduction band (CB), generating positive holes ( $h^+$ ) in the VB, and then the reduction and oxidation half reactions with the electrons and holes will be taken place respectively (Fig. 1a) [47,48]. As for MOFs, the organic linker is regarded as VB and the metallic cluster plays the role of CB (Fig. 1b). Specially, the process for an organic semiconductor is also described as occurring between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [49–51]. The development of pristine MOFs as photocatalysts is from ultraviolet (UV) –light-driven ( $E_g > 3.1$  eV,  $\lambda < 400$  nm) to visible-light-driven ( $E_g < 3.1$  eV,  $\lambda > 400$  nm).

The initial attempts of MOFs utilized in photocatalytic reactions are under UV-light irradiation. The first example of MOFs as a photocatalyst is Mahata and the co-workers' report, in which three new coordination polymers ( $[Co_2(C_{10}H_8N_2)] [C_{12}H_8O(COO)_2]_2$ ,  $[Zn_2(C_{10}H_8N_2)] [C_{12}H_8O(COO)_2]_2$  and  $[Ni_2(C_{10}H_8N_2)_2] [C_{12}H_8O(COO)_2]_2 \cdot H_2O$ ) were examined for the degradation of orange G (OG), rhodamine B (RhB), Remazol Brilliant Blue R (RBBR) and methylene blue (MB) under

the irradiation of mercury vapor lamp [53]. The catalytic activities of three MOFs followed the reverse order to their band gaps. In 2007, Garcia and co-workers studied the photocatalytic properties of MOF-5(Zn) in the degradation of phenol and proved that MOF-5 exhibited reverse shape-selectivity [39,52]. Furthermore, they found the terephthalate linkers could absorb light and sensitized the semiconductor dots. To further investigate the influence of organic linkers on the photocatalytic activity of MOF-5, Gascon and co-workers demonstrated that the band gap energy of metal-organic frameworks can be tuned by changing the organic linker (Fig. 2) [54]. They found that using the 2,6-naphthalenedicarboxylic acid as a linker performed the best catalytic activity in the photooxidation of propene. Although there were other more studies focused on MOF-5 as photocatalysts [52,55], it would

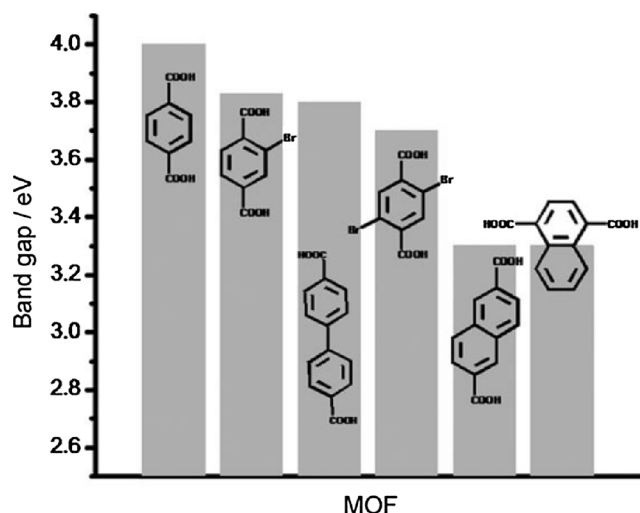


Fig. 2. The band gap value of different linkers of MOFs [54].

suffer structure transformation when exposed to water [56], and this structural change impaired the photocatalytic property. However, water is inevitable in some photocatalytic processes, such as the hydrogen generation in water and wastewater treatment. Therefore, to strengthen the stability of MOFs, especially in water is an important goal.

UiO-66 is a typical water-tolerant Zr-containing MOF. The first report on UiO-66 utilized in photocatalysis was for hydrogen generation in water/methanol upon irradiation at wavelength longer than 300 nm [44]. According to the laser flash photolysis data, the charge separation with electrons in the conduction band happens upon photon absorption. Although the apparent quantum yield was low and the band gap energy of UiO-66 (3.5 eV) is wide, such pioneering work opens ways for various modifications to UiO-66 for visible-light photocatalysis. Later in 2015, a UiO-66-type zirconium MOF using chromophoric anthracene-9, 10-dicarboxylic acid instead of terephthalate acid ( $\text{H}_2\text{BDC}$ ) was synthesized and performed efficiently in the visible-light-driven photocatalytic degradation of MO [57]. Jing and co-workers utilized ZIF-8 for the degradation of MB under UV-light irradiation [58]. They proved that the photocatalytic activity of ZIF-8 could work effectively over a wide pH range, especially in strong alkaline environment. However, the wide band gap of ZIF-8 (5.1 eV) limits the applications for photocatalysis to some degree.

MOFs containing Ti has attracted huge attention. In 2009, MIL-125(Ti) was synthesized by Dan-Hardi and co-workers for the first time [59]. The hybrid material exhibited high photonic sensitivity for the formation of Ti(III)-Ti(IV) mixed valence under UV-vis irradiation in the presence of alcohols, and the reduction of titanium centers and oxidation of absorbed alcohol molecules occurred simultaneously. Recently, MIL-125 was rapidly synthesized via a microwave route by George and co-workers [60]. The MIL-125 had a band gap energy of 3.14 eV and could degrade MB to ca. 96.77% in 6 h under UV-light irradiation.

Although an increasing number of MOFs appeared for photocatalysis, the large band gaps limited their utilization under visible light. It has stimulated researchers to develop novel MOFs with a reduced band gap to enhance the activity under visible-light irradiation. Das and co-workers synthesized a doubly interpenetrated semi-conducting MOF  $\text{Zn}_4\text{O}(\text{2,6-NDC})_3(\text{DMF})_{1.5}(\text{H}_2\text{O})_{0.5}4\text{DMF} \cdot 7.5\text{H}_2\text{O}$  (UTSA-38) for the methyl orange (MO) degradation [61]. The UV-vis diffuse reflective spectra (DRS) of UTSA-38 presented that it is a semiconductor MOF with a band gap of 2.85 eV. MIL-53 is a series of isostructural materials with the same organic linkers but different metal centers including Fe, Al and Cr. Among them, the MIL-53(Fe) possesses a narrow band gap of about 2.72 eV [51]. MIL-53(Fe) performed better photocatalytic activity for MB decolorization both under UV-light and visible-light irradiation. After a few years, MIL-53(Fe) got the further researches in the Cr(VI) reduction, dyes degradation and photoelectrochemical water oxidation under visible-light irradiation [62–64]. As the other typical visible-light responsive MOFs, MIL-100(Fe) has been synthesized for the selective benzene hydroxylation to phenol under visible-light irradiation using  $\text{H}_2\text{O}_2$  as an oxidant (Fig. 3) [65]. A benzene conversion of 30.6% was achieved with a 3:4 ratio of  $\text{H}_2\text{O}_2$ :benzene over MIL-100 after 24 h. According to the ESR results and kinetic studies, the benzene hydroxylation process involved a coupling of Fe-O clusters in MIL-100 with a Fenton-like route. Besides, the structures of MOFs significantly influenced the photocatalytic efficiency. The MIL-100(M) (M = Al, Fe, V, Cr) with different metal centers has also been researched for MB photocatalytic degradation [66].

Although the aforementioned studies were both interesting and important, the MOFs could capture only a fraction of the photons in the visible spectrum. Toward this end, Lee and co-workers developed a pillared-paddlewheel type metal-organic framework featuring bodipy- and porphyrin-based struts, named BOP MOF (Fig. 4) [67]. The two struts in MOFs were a complementary pair of chromophores, in which the bodipy struts served as antenna chromophores for the excitation of

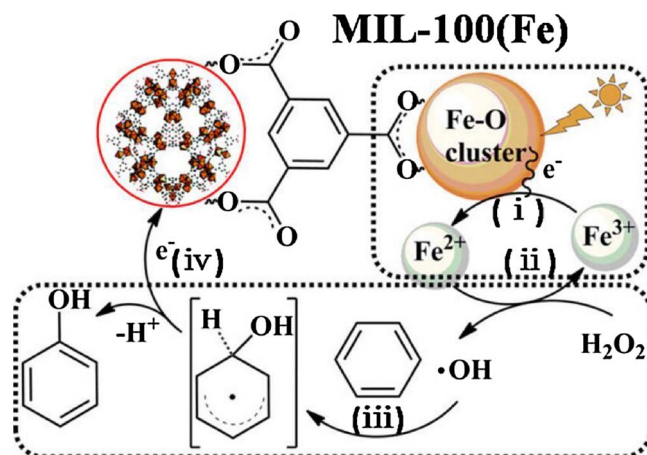


Fig. 3. Reaction mechanism for the photocatalytic benzene hydroxylation over MIL-100 [65].

porphyrinic struts. This BOP MOF could harvest light across the entire visible spectrum. Similarly, to utilize the advantage of small band gap of Iron (III) oxides and overcome the disadvantage of the high electron-hole recombination rate. MOFs containing  $\text{Fe}_3\text{-}\mu_3\text{-oxo}$  clusters were proposed as visible-light photocatalysts with the small particle dimensions and the remarkable photocatalytic efficiency of such Fe(III)-based MOFs were examined for the first time [68]. Later, other Fe(III)-based MOFs have also been investigated as photocatalysts for visible-light-driven  $\text{O}_2$  evolution from water and benzene hydroxylation to form phenol [65,69].

Ti(IV)-based porous NTU-9 displayed stronger absorption in the visible light region than MIL-125 [40]. It shows a broad range of absorption in the visible region from 400 nm to 750 nm with a band gap of 1.72 eV (Fig. 5). The results of density of states (DOS) demonstrated the existence of charge transfer from the organic ligand to Ti(IV) atoms in NTU-9, which further proved the mechanism of ligand-to-metal charge transfer (LMCT) [39,67,70]. Crystalline NTU-9 is stable in air, water and common organic solvents. The photocatalytic activity was tested by the degradation of RhB and MB under visible-light irradiation ( $\lambda > 420$  nm). RhB and MB were completely degraded for 80 min and 20 min, respectively (5 mg of NTU-9 was added in 10 mL of organic dyes ( $10^{-4}$  mol/L)). ZIF-67(Co) also has a broad light absorption, not only in the UV and visible-light region but also in the near IR region. The features were ascribed to the LMCT transition, the higher-lying [ $^4\text{A}_2(\text{F})$ - $^4\text{T}_1(\text{P})$ ] and lower-lying [ $^4\text{A}_2(\text{F})$ - $^4\text{T}_1(\text{F})$ ] d-d ligand field transitions, and  $\text{Co}^{2+}$  ions in  $\text{T}_d$  environment [71]. Optical transient absorption results showed that a long-lived excited state was formed after photo-excitation. Furthermore, the long-lived excited state was confirmed to be the charge-separated state with LMCT character according to X-ray transient absorption spectroscopy [72]. These characters suggested its potential application in heterogeneous photocatalysis [73] and energy conversion.

Pristine MOFs as photocatalysts were also called the “Opportunistic” photocatalysts [36], meaning that this type of photocatalysts are rare and hard to be readily tuned. Furthermore, most of pristine MOFs as photocatalysts are merely sensitive to UV light and the lifetimes of the excited states are too short to perform the catalytic activity, which limited the practicability under solar illumination. Pristine MOFs for photocatalysts and their corresponding applications are listed in Table 1. Besides, the exploitation of new MOFs that response to visible light is a challenging task. Therefore, modifications to MOFs would be a sensible choice.

### 3. UiOs

The rational designs and modifications of MOFs focus on two

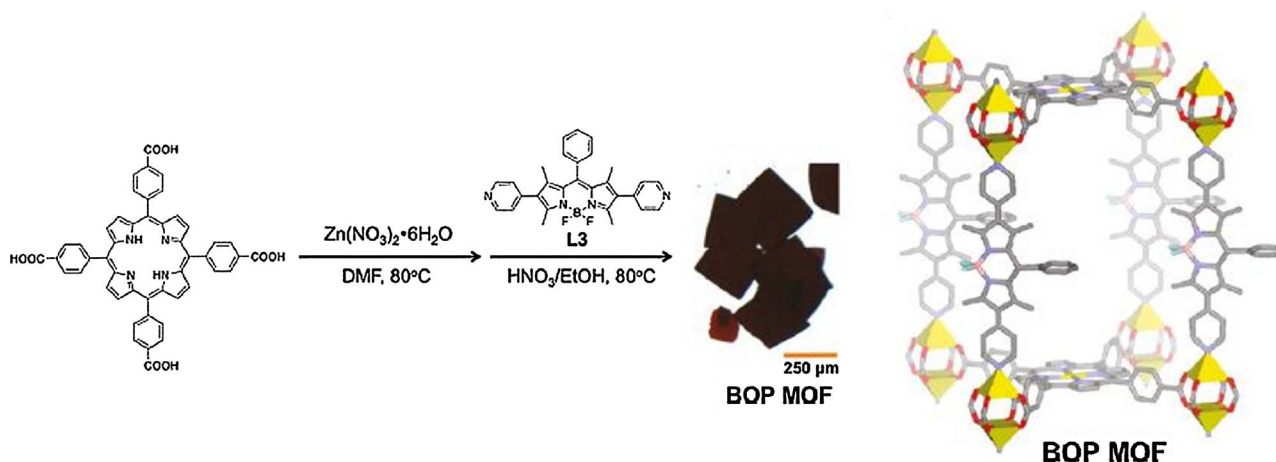


Fig. 4. Synthesis of the BOP MOF and its structure [67].

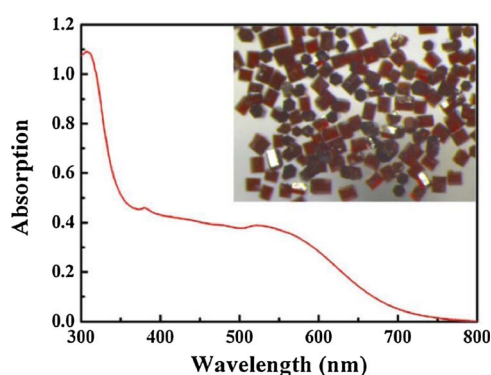


Fig. 5. UV-vis diffuse reflectance spectra of NTU-9 [40].

approaches: (1) Increase the absorption intensity to visible light, and (2) Reduce the recombination rate of the photo-induced electrons and holes. Toward this end, many different strategies have been reported, including decoration of linker or metal center, combination with semiconductors, metal nanoparticles (MNPs) loading, sensitization, pyrolyzation, decoration by GR or RGO and incorporation with functional materials. The modifications of MOFs, including UiOs (mainly UiO-66), MILs (mainly MIL-125, MIL-101, MIL-100 and MIL-53) and ZIFs (mainly ZIF-8 and ZIF-67), and their applications in photocatalysis will be introduced.

Table 1

Pristine MOFs for photocatalysts and their corresponding applications.

| MOF species   | Applications   | Light source    | Year       | Ref.       |
|---|--|-----------------|------------|------------|
| $[\text{Co}_2(\text{C}_{10}\text{H}_8\text{N}_2)][\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2]_2$ , $[\text{Ni}_2(\text{C}_{10}\text{H}_8\text{N}_2)_2][\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2]_2 \cdot \text{H}_2\text{O}$<br>$[\text{Zn}_2(\text{C}_{10}\text{H}_8\text{N}_2)][\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2]_2$ | OG, RhB, RBBr and MB degradation                       | UV              | 2006       | [53]       |
| MOF-5   | Phenol degradation                                     | UV              | 2007, 2008 | [39,52,55] |
| MOFs with changed linkers of MOF-5  | Propylene oxidation                                    | UV              | 2008       | [54]       |
| MIL-125   | Alcohols oxidation, MB degradation                     | UV              | 2009, 2017 | [59,60]    |
| UiO-66  | $\text{H}_2$ production                                | UV              | 2010       | [44]       |
| ZIF-8   | MB degradation   | UV              | 2014       | [58]       |
| MIL-53(M) (M = Fe, Al, Cr)  | MB degradation   | UV-vis, visible | 2011       | [51]       |
| UTSA-38   | MO degradation   | UV-vis          | 2011       | [61]       |
| BOB and BOP MOF   | —  | Visible         | 2011       | [67]       |
| Fe(III)-based MOFs  | Rh6G degradation, $\text{O}_2$ production              | Visible         | 2013, 2016 | [68,69]    |
| NTU-9   | RhB, MB degradation                                    | Visible         | 2014       | [40]       |
| MOFs with changed linkers of UiO-66   | MO degradation   | Visible         | 2015       | [57]       |
| MIL-100, MIL-68   | Benzene hydroxylation                                  | Visible         | 2015       | [65]       |
| MIL-53(Fe)  | Cr(VI) reduction, dyes degradation and water oxidation | Visible         | 2015, 2017 | [62–64]    |
| ZIF-67  | Cr(VI) reduction                                       | UV-vis-NIR      | 2016       | [72,73]    |
| MIL-100(M) (M = Al, Fe, V, Cr)  | MB degradation   | UV              | 2016       | [66]       |

Due to the exceptional water, thermal ( $\sim 500^\circ\text{C}$ ), chemical and mechanical stability [44,74], UiO-66 (UiO = University of Oslo), constructed from Zr secondary-building units (SBUs) and  $\text{H}_2\text{BDC}$ , rapidly becomes the most popular MOF in the area of photocatalysis since its first synthesis by Cavka and co-workers [75]. However, the  $\text{Zr}_6\text{SBU}$ s ( $\text{Zr}_6\text{O}_4(\text{OH})_4$ ) cannot accept electrons from the BDC linker under visible-light irradiation because the redox potential energy level of the  $\text{Zr}_6\text{SBU}$ s in UiO-66 is higher than the LUMO of the BDC linkers, which leads to no visible-light absorption by UiO-66 [76,77]. Thus, modifying UiO-66 as visible-light responsive photocatalysts is extremely necessary. The modifications to UiO-66 focus on the decoration of linker or metal center [44,77–84], combination with semiconductors [41,85–94], MNPs loading [95,96], sensitization [42,43,97] and functionalization by RGO [4,98].

### 3.1. Decoration of linker or metal center

A facile and feasible opportunity to tune optical properties of MOFs lies in the decoration of the organic linkers or metal centers, realizing the control to the chemical and physical properties of photocatalysts at the molecular level. The linker decoration can change the band gap energy of MOFs to some degree [54], which shifts the photo absorption edge from the UV to visible-light region. Silva and co-workers firstly synthesized UiO-66- $\text{NH}_2$  by replacing  $\text{H}_2\text{BDC}$  by 2- $\text{NH}_2$ -terephthalic acid in the synthesis precursor solutions [44]. Compared with UiO-66, UiO-66- $\text{NH}_2$  is a yellow powder and performs a wide absorption from



300 to 440 nm. The amino substituent acts as an auxochromic and bathochromic group in the aromatic ring, leading to the absorption wavelength shift of UiO-66. The quantum yield for  $H_2$  generation was 3.5% by UiO-66-NH<sub>2</sub> under monochromatic light at 370 nm in water/methanol 3:1. Although the quantum yield is still low, the amino decoration to UiO-66 opens a precedent for the subsequent linker decoration. In order to broaden the application scopes and explore the unfilled potential of UiO-66-NH<sub>2</sub>, Wu and co-workers studied the photocatalytic selective oxidation of alcohols to their corresponding aldehydes and reduction of aqueous Cr(VI) utilizing UiO-66-NH<sub>2</sub> as the photocatalyst [78]. UiO-66-NH<sub>2</sub> exhibited photocatalytic activity in the two reactions under visible-light irradiation. To deepen the studies of the fundamental structure-property relations between the organic linker and the band gap of MOFs, Flage-Larsen and co-workers realized band gap modulations of the UiO-66-R (R = H, NH<sub>2</sub>, NO<sub>2</sub>) and the band gap changes could be quantified. They demonstrated that the NH<sub>2</sub> introducing reduced the band gap significantly and the changes not only related to the alters in the linker but also the nonbonding oxygen near the metalloid cluster [99]. Later, the band gap modulation by the same three linker designs (BDC, BDC-NO<sub>2</sub> and BDC-NH<sub>2</sub>) of UiO-66 was investigated via the computation and experimental perspectives [100]. The reduced band gaps of UiO-66-NH<sub>2</sub> (2.75 eV) and UiO-66-NO<sub>2</sub> (2.93 eV) were highly influenced by the bonding nature between the functional group and the aromatic carbon ring, which was confirmed by the time-dependent density functional calculations. The above-mentioned two studies confirmed the linker decoration by NH<sub>2</sub> group for UiO-66 possesses the smallest band gap, which make the UiO-66-NH<sub>2</sub> a popular material for the various catalytic studies. Recently, a Zr-MOF-FePC decorated by 2-pyridinecarboxaldehyde (PC) and FeCl<sub>3</sub>·6H<sub>2</sub>O based on UiO-66-NH<sub>2</sub> was synthesized through combined covalent and dative post-synthetic modification [101]. The new multifunctionalized Zr-MOF can act as both a photocatalyst (Zr-oxo cluster), and a catalyst (Fe(III) in addition to Zr(IV) sites) for one-pot tandem photo-oxidative Passerini three-component reaction of alcohols.

Following this research direction, a series of mixed-linker Zr-based MOFs have been synthesized in one pot reactions for the visible-light photocatalytic oxidation of alcohol by Goh and co-workers [79]. The mixed-linker Zr-MOFs containing two linkers: (1) Primary linker: 2-amino-1,4-benzenedicarboxylate (NH<sub>2</sub>-BDC) and (2) secondary linker: 2-X-1,4-benzenedicarboxylate (X-BDC, X = H, F, Cl, Br). Results revealed that the Zr-MOF containing mixed NH<sub>2</sub>-BDC and F-BDC linkers performed five times more conversion compared to the Zr-MOF made of mixed NH<sub>2</sub>-BDC and H-BDC linkers in the oxidation of benzyl alcohol. The enhanced photocatalytic activity was attributed to the partial substitution of the primary NH<sub>2</sub>-BDC by electron-withdrawing halogenated BDC linkers. However, the effect of mixed linkers on the band gap of the Zr-MOFs was not researched comprehensively. To elucidate the effects of linker functional groups on the photoabsorption properties of UiO-66-X materials, a combined theoretical and experimental study were carried out by Hendrickx et al. [80]. The computed electronic properties of the periodic UiO-66 revealed that the band gap could be altered by linker functionalization and ranged from 4.0 to 2.2 eV (Fig. 6), suggesting the linker functionalization is indeed a promising way to modify the band gap of MOFs. They also proved that the bi-substituted linkers show smaller band gap energy than the mono-substituted linkers in the UiO-66.

The exchange of metal center of MOFs used to show no effect on the photocatalytic activity [51,52]. However, new findings suggested that partial substitution of metal center could influence the photocatalytic activity in a certain degree [77,82–84,102]. Metal doping becomes to be an effective way for enhancing the performance of semiconductor-based photocatalysts [103,104]. Constructing bimetallic assemblies by partial metal substitution brought out an enhanced photocatalytic performance particularly under visible light, because of the introduction of metal-to-metal charge transfer. The partial substitution of metal cations in MOFs can result in the formation of oxo-bridged hetero-

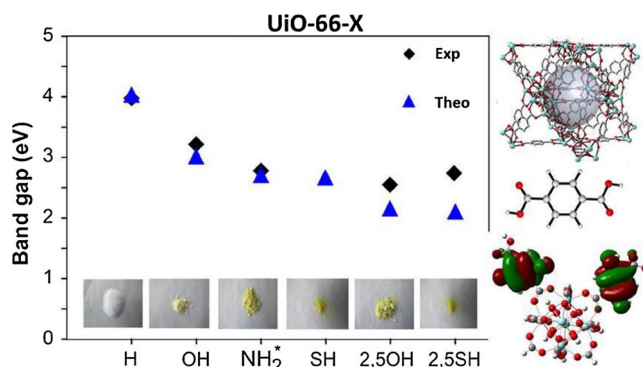


Fig. 6. The band gap of different linker-functional UiO-66 and its structure [80].

metallic assemblies within the same MOFs [105,106]. Such bimetallic assemblies, similar to those constructed over zeolites and semiconductors but with more flexibility and tenability owing to the availability of different structures of MOFs, are expected to show enhanced photocatalytic performance [82]. Li and co-workers demonstrated that the construction of the bimetallic assembly through the metal center substitution in MOFs was an efficient way to improve the photocatalytic activity of MOFs in 2014 [82]. They synthesized the Ti substituted UiO-66-NH<sub>2</sub> by a post-synthetic exchange (PSE) method and investigated its photocatalytic performance on the photocatalytic CO<sub>2</sub> reduction and H<sub>2</sub> production. The enhanced photocatalytic activity was due to that the introduced Ti substituent played a role of mediator to facilitate electron transfer according to the density functional theory (DFT) calculations and electron spin resonance (ESR) results. As shown in Fig. 7, the photo-excited electrons were produced when visible light irradiated on 2-aminoterephthalic acid (ATA) and then transferred to the Ti/Zr-O oxo-metal cluster (Ti/Zr)<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> of Ti substituted UiO-66-NH<sub>2</sub>. The photo-excited electrons were eager to transfer to Ti<sup>4+</sup> rather than Zr<sup>4+</sup> according to theoretical studies. Thus the intermediate (Ti<sup>3+</sup>/Zr<sup>4+</sup>)<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> was formed and acted as an electron donor that donated electrons to Zr<sup>4+</sup> to form Ti<sup>4+</sup>-O-Zr<sup>3+</sup>. As a result, the efficiency of interfacial charge transfer from ATA to Zr-O oxo-clusters was improved, leading to the enhanced photocatalytic activity. After that, the research group utilized the same method and prepared different amounts of Ti substituted UiO-66-NH<sub>2</sub> [83]. The transient absorption spectroscopy was studied systematically and a new application in photovoltaic cell was carried out. A perfect circle was provided and the Ti substituted UiO-66-NH<sub>2</sub> (NH<sub>2</sub>-UiO-66(Zr/Ti)) reached a higher photon-to-current efficiency than UiO-66-NH<sub>2</sub>.

Based on the above-mentioned work, more studies were carried out [77,84,102]. Lee introduced diamine-substituted ligands on the Ti substituted UiO-66-NH<sub>2</sub> via the PSE method (Fig. 8) for CO<sub>2</sub> reduction to HCOOH under visible-light irradiation [77]. Ti substitution decreased the electron accepting levels and the diamine-substituted ligands introduction offered new energy levels for additional light absorption and charge transfer, which is responsible for the enhanced photocatalytic activity. Yasin and co-workers demonstrated that the smallest band gap of partial Ti substituted UiO-66-NH<sub>2</sub> was UiO-66 (Ti<sub>5</sub>Zr<sub>1</sub>)-NH<sub>2</sub> (metal cluster: Ti<sub>5</sub>Zr<sub>1</sub>O<sub>4</sub>(OH)<sub>4</sub>) (2.60 eV) [102]. For the purpose of improving synthetic efficiency of Ti substituted UiO-66-NH<sub>2</sub>, a microwave-assisted method was developed by Tu et al. [84]. The Ti substituted UiO-66-NH<sub>2</sub> could be prepared within a few hours rather than several days and the crystallinity well maintained. The prepared Ti substituted UiO-66-NH<sub>2</sub> showed enhanced photocatalytic activity for the photochemical vapor generation system to reduce Se(VI).

The decoration at molecular level (linker and metal center) to improve the photocatalytic activity of UiO-66 under visible-light is quite feasible. However, the choices of organic linkers modification and suitable substituted metal center are limited. Moreover, the separation efficiency of electrons and holes is incapable to be controlled. Other

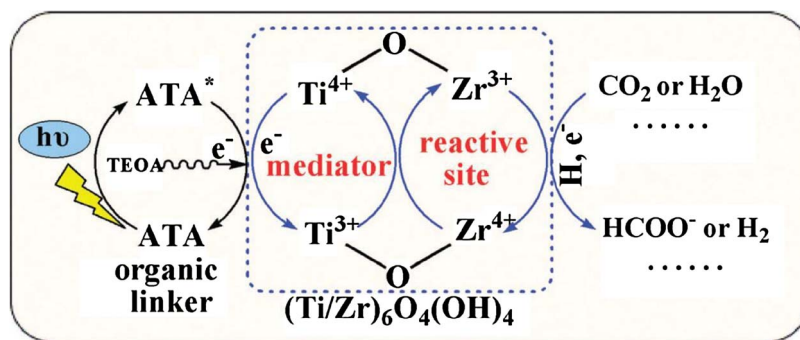


Fig. 7. Proposed enhanced mechanism for the photocatalytic reactions over Ti substituted UiO-66-NH<sub>2</sub> [82].

new strategies for improving the photocatalytic activity of UiO-66 are expected.

### 3.2. Combination with semiconductors

Compared to the method of linker or metal center decoration, an relatively ideal solution is to assemble UiO-66 with narrow band gap semiconductors to form heterogeneous photocatalysts [92]. There are two advantages: (1) the enlarged light absorption edge covering the visible-light area after the combination, leading to much narrower band gap compared to UiO-66 or UiO-66-NH<sub>2</sub>. (2) The enhanced separated efficiency of photo-induced electrons and holes due to the appearance of electron transfer between semiconductors and UiO-66 or UiO-66-NH<sub>2</sub>.

As a typical and important class of the II-VI semiconductor, CdS has been studied intensively and widely as practically applicable material in photocatalysis over the past decades owing to its narrow band gap (2.4 eV) as well as the size-dependent electronic and optical properties [107]. However, pure CdS particles have several issues that limit its utilization, including the aggregation of particles, high recombination rate of photogenerated electron-hole pairs and the property of photo-corrosion [108]. Therefore, anchoring CdS on MOFs is a promising choice to avoid the above mentioned problems. The CdS nanorods on UiO-66-NH<sub>2</sub> were realized by a facile room-temperature photodeposition and such nanocomposites behaved high photocatalytic activity for selective oxidation of alcohol (Fig. 9) [41]. The optical band gap of CdS-UiO-66(NH<sub>2</sub>) and the amount of generated rodlike CdS could be tuned by changing the irradiation time during the CdS photodeposition. UiO-

66-NH<sub>2</sub> served not only as the support but also as the electrons provider to trigger the reaction for coupling itself with metal sulfides. Later, CdS was also loaded on UiO-66 by Zhou and co-workers through a hydro-thermal process in 2015 [87]. The resulting CdS/UiO-66 hybrid composites exhibited remarkably active H<sub>2</sub> production under visible-light irradiation as compared to CdS and UiO-66, which is ascribed to the effective separation of photo-induced electrons and holes across the composites.

Sheet-like structure materials, such as RGO and MoS<sub>2</sub>, incorporated on UiO-66/CdS could enhance the interfacial interaction between UiO-66 and CdS, leading to the improved charge transfer efficiency. Wu's group designed a ternary composite by introducing RGO to the UiO-66/CdS composite [85]. The introduction of RGO offers more efficient charge separation than that of binary system (UiO-66/CdS) according to the electrochemical impedance spectroscopy analysis. The prepared UiO-66/CdS/1%RGO performed a photocatalytic H<sub>2</sub> production rate 13.8 times as high as that of pure commercial CdS, and exhibited much higher photocatalytic efficiency than the inorganic semiconductor material — P25/CdS/1%RGO under visible light. The other ternary composite MoS<sub>2</sub>/UiO-66/CdS was also developed by Wu and co-workers [86]. MoS<sub>2</sub> as cocatalyst was deposited on UiO-66/CdS by a facile photo-assisted approach and the obtained composites possessed an intimate interfacial interaction among CdS, UiO-66 and MoS<sub>2</sub>. The H<sub>2</sub> production rate could reach 650 μmol h<sup>-1</sup> when the content of UiO-66 was 50 wt% and MoS<sub>2</sub> was 1.5 wt%, which was nearly 60 times higher than that of pure CdS. Cd<sub>x</sub>Zn<sub>1-x</sub>S solid solutions are promising materials because ZnS possesses the same coordination mode with CdS [109]. The band gap energy of the solid solution can be flexibly altered

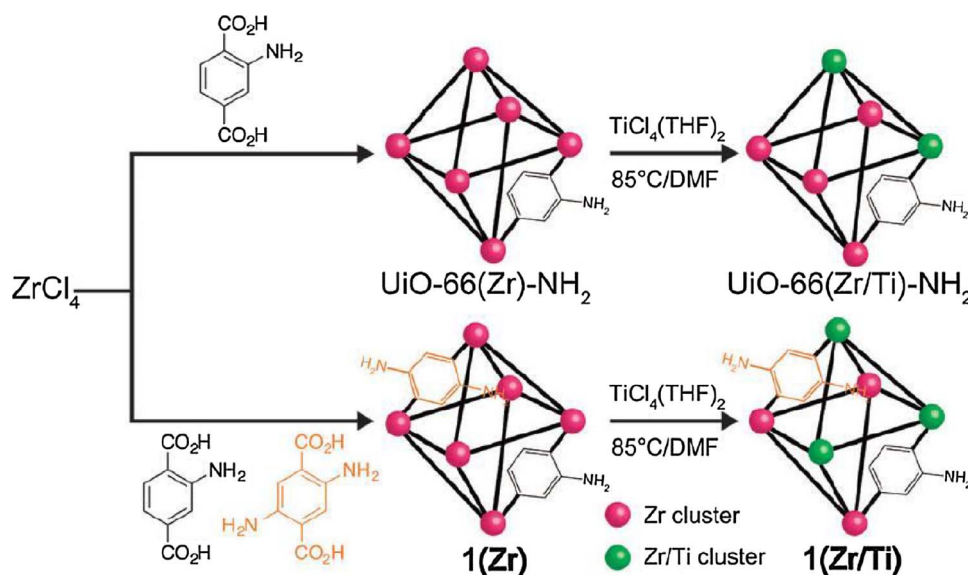


Fig. 8. Synthesis of mixed-metal MOFs 1(Zr) via PSE to obtain mixed metal MOFs 1(Zr/Ti), UiO-66(Zr/Ti)-NH<sub>2</sub> [77].

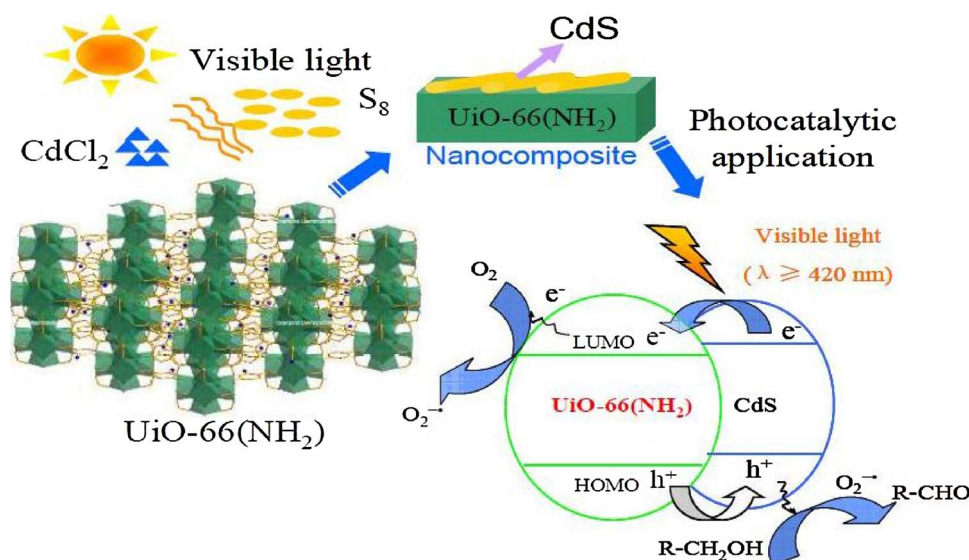


Fig. 9. The photodeposition of CdS on UiO-66(NH<sub>2</sub>) and its application for photocatalytic oxidation of alcohol [41].

by changing the molar ratio of CdS and ZnS [110]. Su and co-workers synthesized a highly active Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composite photocatalysts by a facile solvothermal process for the H<sub>2</sub> production and CO<sub>2</sub> reduction under visible light. The H<sub>2</sub> and CH<sub>3</sub>OH production rate could reach 5846.5 and 6.8 μmol h<sup>-1</sup> g<sup>-1</sup> respectively with 20 wt% content of UiO-66-NH<sub>2</sub>, which were much higher than that of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and UiO-66-NH<sub>2</sub>. Inspired by their original work, our group chose ZIF-8 instead of UiO-66-NH<sub>2</sub> to load Cd<sub>0.5</sub>Zn<sub>0.5</sub>S for the Cr(VI) photocatalytic reduction [111]. The existence of S-Zn bond between Cd<sub>0.5</sub>Zn<sub>0.5</sub>S and ZIF-8 highly improved the photocatalytic activity and stability of Cd<sub>0.5</sub>Zn<sub>0.5</sub>S@ZIF-8 composites.

Recently, bismuth-based semiconductors attracted extensive attention due to their narrow band gap energy (BiOBr: 2.8 eV, Bi<sub>2</sub>MoO<sub>6</sub>: 2.6 eV) [91,93], great availability, non-toxicity and chemical inertness [112]. Three types of bismuth-based semiconductor: Bi<sub>2</sub>WO<sub>6</sub>, BiOBr and Bi<sub>2</sub>MoO<sub>6</sub> are combined with UiO-66 for the photocatalytic degradation of RhB under visible-light irradiation [89,91,93]. UiO-66 was incorporated with Bi<sub>2</sub>WO<sub>6</sub> via a simple hydrothermal method by Sha and co-workers [89]. The active species involved in the degradation process were investigated by introducing different scavengers, and the results implied that ·O<sub>2</sub><sup>-</sup> and h<sup>+</sup> were two main active species in the photocatalytic degradation of RhB. Bi<sub>2</sub>MoO<sub>6</sub>/UiO-66 composites were synthesized via electrostatic interaction induced self-assembly process between Bi<sub>2</sub>MoO<sub>6</sub> and UiO-66 by Ding and co-workers in 2017 [93]. These above mentioned bismuth-based-semiconductors incorporating with UiO-66 consistently demonstrated that the photo-induced ·O<sub>2</sub><sup>-</sup> and h<sup>+</sup> were the main active species in the photocatalytic degradation of RhB.

Other types semiconductor as outer antenna incorporating with UiO-66 have been extensively studied, such as, g-C<sub>3</sub>N<sub>4</sub> [92], Ag<sub>2</sub>CO<sub>3</sub> [90], AgI [113], CdSe [114], zinc phthalocyanine [94], MoS<sub>2</sub> [115], TiO<sub>2</sub> [116] and polyaniline [117]. Most of them possess a narrow band gap that could absorb visible light abundantly, and UiO-66 or UiO-66-NH<sub>2</sub> not only acts as a perfect substrate, but also a semiconductor to accept or transfer the photo-induced electrons. Thus the separation efficiency of electron-hole pairs will be improved, leading to an enhanced photocatalytic activity. Graphitic carbon nitride, a stable, metal-free and visible-light active photocatalyst, has attracted intensive attention as photocatalysts in different fields [118,119]. In 2015, Shi and co-workers prepared a UiO-66/CNNS (carbon nitride nanosheet) hybrid structure by electrostatic self-assembly of negatively charged CNNS with positively charged UiO-66 [92]. This is the first time that a MOF/CNNS hybrid structure was prepared by electrostatic self-

assembly. They demonstrated that the photo-excited electrons could transfer from CNNS to UiO-66 in UiO-66/CNNS, leading to a much higher photocatalytic activity for the CO<sub>2</sub> conversion than that of bare CNNS. To improve the photocatalytic activity and stability of pristine Ag<sub>2</sub>CO<sub>3</sub>, UiO-66 was incorporated with Ag<sub>2</sub>CO<sub>3</sub> via a convenient solution method by Sha and co-workers [90]. The prepared Ag<sub>2</sub>CO<sub>3</sub>/UiO-66 showed enhanced photocatalytic activity for RhB degradation compared to the physical mixture of UiO-66 and Ag<sub>2</sub>CO<sub>3</sub> under visible-light illumination. This was ascribed to more Ag<sub>2</sub>CO<sub>3</sub> active sites on the composite surface. By virtue of the advantages of metal center partial substitution of UiO-66, Xu and co-workers incorporated polyaniline (PANI) with FeUiO-66 (iron doped UiO-66) by annealing process [117]. The photocatalytic performance were evaluated by the selectively oxidation of various alcohol under visible-light irradiation using molecular oxygen as a benign oxidant. The superior photocatalytic activity of PANI/FeUiO-66 nanohybrids was ascribed to valence fluctuation of Fe<sup>2+</sup>/Fe<sup>3+</sup> and formed heterostructures between PANI and UiO-66, which could enhance the separation efficiency of photogenerated carriers. Moreover, the major contributors to the oxidation of alcohols were ·O<sub>2</sub><sup>-</sup> and h<sup>+</sup>, which was proved as well. Combination with semiconductors is the most commonly used strategies to modify MOFs for photocatalysis, but seeking a very ideal semiconductor for greatly improving the activity and practicability is still a big challenge.

### 3.3. MNPs loading

MNPs attracted enormous attention in the past decade because of their great potential in different kinds of applications, especially in catalysis [120]. Size shrinkage of the particles to nanoscale can significantly enhance their catalytic efficiency due to the high surface-to-volume ratio, great ratio of atoms remaining at the large surface area, and the high density of the coordination unsaturated sites [121]. As for photocatalytic reactions, metal loading scarcely improves the absorption of visible light, which means that the little red-shift for the materials is derived from the color change [96]. Metals of Au, Ag, and Cu could increase the light absorption via the localized surface plasmon resonance (LSPR) under visible-light irradiation. Pd NPs of about 3–6 nm in diameter were highly dispersed and immobilized in UiO-66-NH<sub>2</sub> via a facile one-pot hydrothermal method by Wu's research group [95]. Due to the high dispersion of Pd NPs and their close contact with UiO-66-NH<sub>2</sub>, the resulting Pd@UiO-66-NH<sub>2</sub> was utilized as a highly efficient bifunctional photocatalyst to remove Cr(VI) and dyes simultaneously. Cr(VI) reduction by electrons (e<sup>-</sup>) and dyes oxidation by



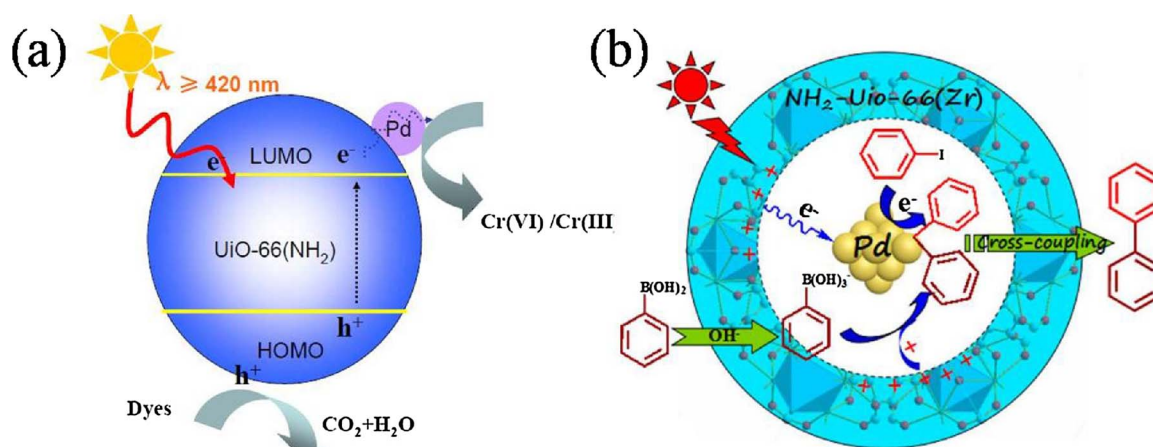


Fig. 10. Proposed mechanism of the visible-light catalytic remove of Cr(VI) and dyes [95] (a) and Suzuki Coupling Reaction over Pd@UiO-66-NH<sub>2</sub> [96] (b).

holes ( $h^+$ ) occurred in the both ends of LUMO and HOMO in UiO-66(NH<sub>2</sub>) (Fig. 10a), which highly promoted the two reactions simultaneously. The Pd NPs accepted the photo-excited electrons from UiO-66-NH<sub>2</sub> to reduce Cr(VI). Later, smaller Pd nanoclusters (< 1.2 nm) were encapsulated inside the cage of UiO-66-NH<sub>2</sub> via a double-solvent approach followed with a photoreduction process [96]. The resulting Pd@UiO-66-NH<sub>2</sub> performed efficiently in the visible-light-promoted Suzuki coupling reaction (Fig. 10b). Two factors contributed to the significantly enhanced photocatalytic activity, one is the presence of abundant coordinated unsaturated active Pd sites, the other is the efficient photo-excited electrons transfer from UiO-66-NH<sub>2</sub> to the confined Pd nanoclusters.

Up to now, research into MNPs loading on the UiO-66 for photocatalysis is rare. Because the MNPs (except Au, Ag and Cu) loading can not increase the visible-light absorption. They majorly served as electron acceptor and mediator and the substrate need to absorb visible light. Thus the substrate is always based on visible-light responsive MOFs, such as UiO-66-NH<sub>2</sub>.

### 3.4. Sensitization

Since the first study of dye-sensitized colloidal TiO<sub>2</sub> films with an enhanced light-to-electric energy conversion yield in 1991 [122], dye-sensitization has become a relatively mature technology for the red shift of semiconductor photocatalysts to enhance the visible-light harvesting. In addition, given both partial MOFs (the organic linker contains benzene ring, e.g. UiO-66 and MIL-125) and dyes containing benzene ring, it is expected that a strong  $\pi$ - $\pi$  stacking and Van Der Waals interaction formation between MOFs and dyes, which is significant for the efficient charge transfer in a dye-sensitized photocatalyst system. Thus, MOFs decorated by dye sensitization as photocatalysts are accessible and feasible. He and co-workers reported that Pt@UiO-66 sensitized by adsorbed or directly added RhB dye showed enhanced photocatalytic activity for H<sub>2</sub> production under visible-light illumination in 2014 [42]. The absorption intensity of Pt@UiO-66 in the visible-light region was significantly improved after RhB sensitization, the spectra in 450–600 nm was similar to that of RhB, and RhB absorbed the light and transformed into RhB\*. Meanwhile, the photo-excited electrons transferred to the LUMO of UiO-66 and then a series of reaction happened (Fig. 11). The adsorbed and directly added RhB dye sensitized Pt@UiO-66 extremely enhanced the photocatalytic efficiency to 30 and 26 times as high as that of bare Pt@UiO-66, respectively. Limited for the poor photostability of RhB [123], the low cost Erythrosin B (ErB) dye sensitized UiO-66 has been prepared by Yuan and co-workers for photocatalytic H<sub>2</sub> production under visible-light irradiation [43]. The highest H<sub>2</sub> production rate was 4.6  $\mu\text{mol h}^{-1}$  which occurred from the system containing 10 mg of MOFs photocatalyst and 30 mg ErB with the Pt as a

cocatalyst. The dye sensitized UiO-66-NH<sub>2</sub> was also carried out using a diazo-coupling reaction by Ota and co-workers [97] in 2016. The diazo-coupling reactions of UiO-66-NH<sub>2</sub> with naphthols and aniline yielded reddish samples, and diphenylamine yielded dark violet ones, resulting in a huge red-shift of the optical absorption of UiO-66-NH<sub>2</sub> [97]. The expanded absorption edge of dye sensitized UiO-66-NH<sub>2</sub> confers the higher photocatalytic activity than that of traditional TiO<sub>2</sub> for the degradation of MB.

Given the low cost and easy operation of dye sensitization to MOFs, these studies provide a potential approach to developing highly efficient and practical MOF-based photocatalysts for hydrogen production and environmental remediation. However, it is noticed that the stability of dyes is very important, or else it will bring secondary pollution.

### 3.5. Decoration by RGO

Reduced graphene oxide (RGO) has been considered as an ideal component for fabricating various functional composite materials because of its superior physicochemical properties [124]. In addition, RGO can act as an electron sink to accept the photo-excited electrons from semiconductor that will inhibit the recombination of electrons and holes. However, similar to the MNPs loading, combination with RGO can not increase the visible-light absorption [4,98]. Thus, the RGO decoration is depending on the substrate that could absorb visible light, and UiO-66-NH<sub>2</sub> is the common choice as well. Wu and co-workers assembled RGO/UiO-66-NH<sub>2</sub> nanocomposites by an electrostatically derived self-assembly of the positively charged UiO-66-NH<sub>2</sub> and the negatively charged GO in water [4]. After a hydrothermal reduction process, the obtained RGO/UiO-66-NH<sub>2</sub> nanocomposites showed significantly enhanced visible-light photocatalytic activity for Cr(VI) reduction. In order to fully utilize the superiority of the two-dimensional sheet structure of RGO, a layered sandwich-like hierarchical nanoarchitecture of photoactive RGO/UiO-66-NH<sub>2</sub> was fabricated via a noncovalent methodology for graphene functionalization and a solvothermal synthesis (Fig. 12a) [98]. The pyrene<sup>+</sup>, an amphiphilic pyrene derivative, acted as stabilizer and connector between RGO and UiO-66-NH<sub>2</sub>, leading to an intimate contact between them. The unique sandwich-like heterostructure could promote the separation and transfer of photo-excited charges, leading to the enhanced photocatalytic activity for the selective photocatalytic oxidation of benzyl alcohol under visible-light irradiation (Fig. 12b).

UiO-66 is the most typical and popular MOFs utilized until today due to its excellent photocatalytic properties. Although, the independent research of linker or metal center decoration, combination with semiconductors, MNPs loading, sensitization and decoration by RGO are tremendous, the cross-over studies among these modified methods are likely to be the major direct for the further investigation of



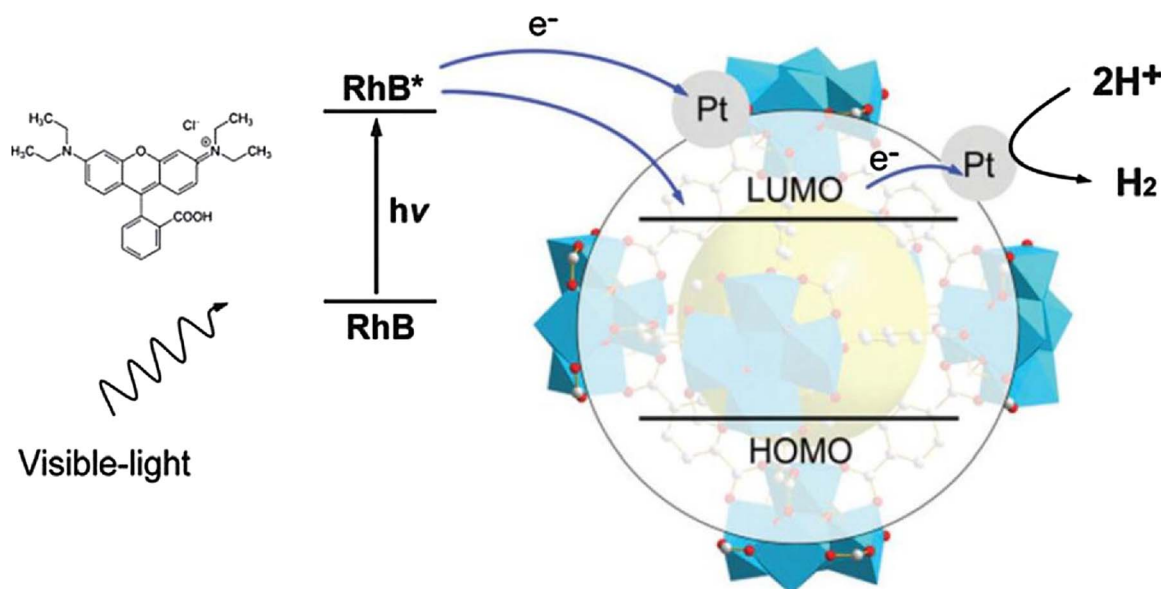


Fig. 11. Proposed mechanism of photocatalytic  $\text{H}_2$  production over RhB-sensitized Pt@UiO-66 under visible-light irradiation [42].

UiO-66 and the brilliant designs of ternary or multi-system are expected. The modified strategies of UiO-66 and their corresponding applications are listed in Table 2.

#### 4. MILs

MILs including MIL-125, MIL-101, MIL-100 and MIL-53 have been widely applied in photocatalysis. Among them pristine MIL-125 is responsive to UV-light irradiation, whereas pristine MIL-101, MIL-100 and MIL-53 are visible-light responsive MOFs.

##### 4.1. Ti-based MIL-125

Titanium is a very attractive candidate element for the design of photocatalysts due to its low toxicity, redox activity and photocatalytic properties. MIL-125 ( $\text{Ti}_8\text{O}_8(\text{OH})_4(\text{BDC})_6$ , MIL = Materials of Institut Lavoisier) constructed from titanium-oxo-hydroxo clusters and  $\text{H}_2\text{BDC}$  linkers was synthesized in 2009 [59]. MIL-125 is thermally robust up to  $360^\circ\text{C}$ , which is fundamental for the design of photocatalysts under a certain temperature. However, similar to UiO-66, MIL-125 possesses a wide band gap energy of 3.6 eV [125], suggesting that the MIL-125 can be merely excited by UV-light irradiation and the separation efficiency of photo-induced charge carriers is low. Thus, the modification to MIL-

125 as photocatalysts is necessary.

##### 4.1.1. Decoration of linker

Decoration of a linker and partial substitution of metal centers are two typical ways of UiO-66 decorated at the molecule level. However, as for MIL-125, there is merely linker decoration to enhance its photocatalytic activity, no report about the metal center partial substitution, and it is probably because the metal center Ti of MIL-125 is an excellent catalytic sites and substitution of other metal is likely to decrease the catalytic activity. In the studies of linker decoration of MIL-125, the introduction of  $\text{NH}_2$  groups in BDC linker still played the major role. MIL-125 shows an absorption edge to 350 nm corresponding to the absorption of Ti-O oxo-clusters. MIL-125- $\text{NH}_2$  shows an extra absorption band in the visible-light region with the absorption edge around 550 nm, which is ascribed to the ligand-based absorption. The visible-light absorption is ascribed to the conjugated  $\pi$  electron transition from the amine containing chromophores to the Ti-oxo clusters. Li and co-workers firstly utilized MIL-125- $\text{NH}_2$  for the photocatalytic reduction of  $\text{CO}_2$  to  $\text{HCOO}^-$  under visible-light irradiation in 2012 [45]. Although the efficiency of the reduction of  $\text{CO}_2$  over MIL-125- $\text{NH}_2$  photocatalyst was low, this work signified that MOFs as photocatalysts hold great promise for the reduction of  $\text{CO}_2$ . Later on, they used MIL-125- $\text{NH}_2$  for the aerobic selective oxidation of amines to imines under visible-light

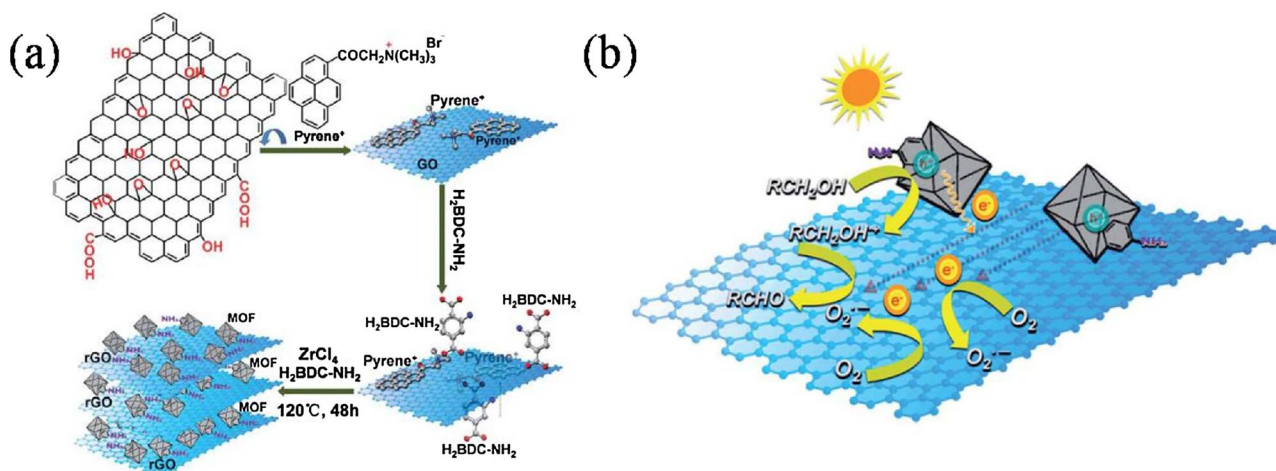
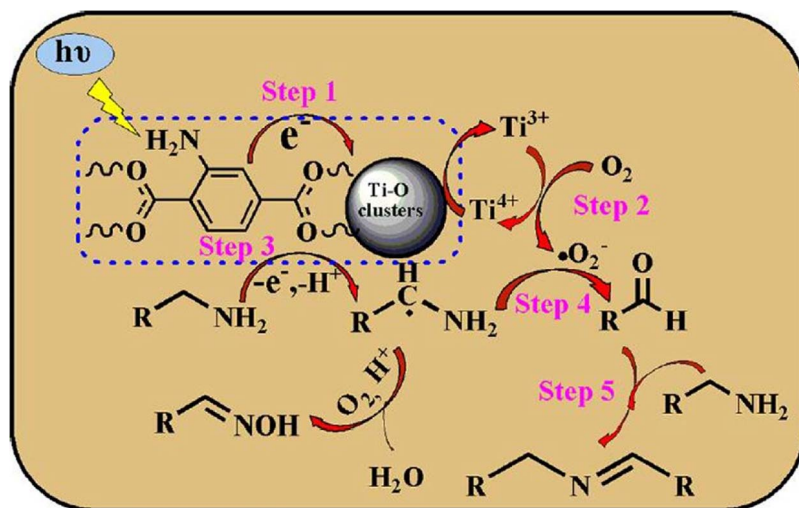


Fig. 12. Fabrication procedures of the layered RGO/UiO-66- $\text{NH}_2$  hybrids (a) and proposed mechanism for the enhanced photocatalytic oxidation over RGO/UiO-66- $\text{NH}_2$  hybrids (b) [98].

**Table 2**  
Modified strategies of UiO-66 and their corresponding applications.

| Strategies                             | details                                 | MOF                       | Applications  | Light source | Ref.       |
|--|---|---------------------------|---|--------------|------------|
| Decoration of metal centers or linkers | -NH <sub>2</sub>                        | UiO-66                    | H <sub>2</sub> production                               | UV           | [44]       |
|  | -NH <sub>2</sub>                        | UiO-66                    | Alcohol oxidation, Cr(VI) reduction                     | Visible      | [78]       |
|  | -F, Cl, Br                              | UiO-66                    | Alcohols oxidation                                      | Visible      | [79]       |
|  | -NH <sub>2</sub> , NO <sub>2</sub> , Br | UiO-66                    | Cr(VI) reduction  | UV-vis       | [81]       |
|  | Ti substitution                         | UiO-66-NH <sub>2</sub>    | Cr(VI), CO <sub>2</sub> reduction, cell.                | Visible      | [77,82,83] |
|  | Ti substitution                         | UiO-66                    | Se(VI) reduction  | UV           | [84]       |
| Combination with semiconductors        | CdS                                     | UiO-66-NH <sub>2</sub>    | Alcohols oxidation                                      | Visible      | [41]       |
|  | CdS                                     | UiO-66                    | H <sub>2</sub> production                               | Visible      | [87]       |
|  | CdS                                     | GO/UiO-66                 | H <sub>2</sub> production                               | Visible      | [85]       |
|  | MoS <sub>2</sub> /CdS                   | UiO-66                    | H <sub>2</sub> production                               | Visible      | [86]       |
|  | Cd <sub>0.5</sub> Zn <sub>0.5</sub> S   | UiO-66-NH <sub>2</sub>    | CO <sub>2</sub> reduction and H <sub>2</sub> production | Visible      | [88]       |
|  | CdSe                                    | UiO-66                    | RhB degradation   | Visible      | [114]      |
|  | Bi <sub>2</sub> WO <sub>6</sub>         | UiO-66                    | RhB degradation   | Visible      | [89]       |
|  | BiOBr                                   | UiO-66                    | RhB degradation   | Visible      | [91]       |
|  | Bi <sub>2</sub> MoO <sub>6</sub>        | UiO-66                    | RhB degradation   | Visible      | [93]       |
|  | AgCO <sub>3</sub>                       | UiO-66                    | RhB degradation   | Visible      | [90]       |
|  | g-C <sub>3</sub> N <sub>4</sub>         | UiO-66                    | CO <sub>2</sub> reduction                               | Visible      | [92]       |
|  | AgI                                     | UiO-66                    | RhB degradation   | Visible      | [113]      |
|  | TiO <sub>2</sub>                        | UiO-66-NH <sub>2</sub>    | CO <sub>2</sub> reduction                               | UV-vis       | [116]      |
|  | MoS <sub>2</sub>                        | GO/UiO-66-NH <sub>2</sub> | H <sub>2</sub> production                               | Visible      | [115]      |
|  | ZnTCPc                                  | UiO-66-NH <sub>2</sub>    | MB degradation  | Visible      | [94]       |
|  | PANI                                    | FeUiO-66                  | Alcohols oxidation                                      | Visible      | [117]      |
| MNPs loading                           | Pd                                      | UiO-66-NH <sub>2</sub>    | Cr(VI) reduction, dyes degradation                      | Visible      | [95]       |
|  | Pd                                      | UiO-66-NH <sub>2</sub>    | Suzuki coupling reaction                                | Visible      | [96]       |
| Sensitization                          | RhB                                     | Pt/UiO-66                 | H <sub>2</sub> production                               | Visible      | [42]       |
|  | ErB                                     | Pt/UiO-66                 | H <sub>2</sub> production                               | Visible      | [43]       |
|  | Naphthols, aniline and diphenylaniline  | UiO-66-NH <sub>2</sub>    | MB degradation  | UV-vis       | [97]       |
| Decoration by RGO                      | RGO                                     | UiO-66-NH <sub>2</sub>    | Cr(VI) reduction  | Visible      | [4]        |
|  | RGO                                     | UiO-66-NH <sub>2</sub>    | Alcohols oxidation                                      | Visible      | [98]       |



**Fig. 13.** The proposed photocatalytic process of the photocatalytic amines oxidation over MIL-125-NH<sub>2</sub> [126].

irradiation and the proposed photocatalytic process was showed in Fig. 13, which clearly exhibited the transfer route of photo-excited electrons [126]. Very recently, in order to deeply study the relationship between the catalytic performances and the amount of functionalized linkers of MIL-125-NH<sub>2</sub>, Chambers and co-workers assessed the photocatalytic activity for the oxidation of benzyl alcohol to benzaldehyde with the increasing amounts of BDC-NH<sub>2</sub> linkers (0%, 20%, 46%, 70% and 100%) incorporated in the framework [127]. Results demonstrated the maximum photocatalytic activity was ~50% BDC-NH<sub>2</sub> content incorporating into the framework, which was ascribed to the occurrence of the mixed valence Ti<sup>4+</sup>-Ti<sup>3+</sup> state within the Ti<sub>8</sub>-wheels in crystal structure of MIL-125. The two studies both verified the switch between Ti<sup>4+</sup> and Ti<sup>3+</sup> of MIL-125-NH<sub>2</sub> in the photocatalytic process. The spectroelectrochemistry and ultrafast spectroscopy have proved that the electron is located in the Ti-oxo clusters and the hole resides in the

amino terephthalate unit particularly the amino group upon photo-excitation [128], which further improved the route of electron transfer in the photo-excited MIL-125-NH<sub>2</sub>. The other photocatalytic applications utilizing MIL-125-NH<sub>2</sub> as catalyst were also been reported, such as the photocatalytic reduction of Cr(VI) [129], photoredox synthesis of N-hydroxy-oxazolidinones [130] and photochemical vapor generation (PCVG) for determination of selenium [131].

Hendon and co-workers explored the diaminated linker BDC-(NH<sub>2</sub>)<sub>2</sub> and other functional groups (-OH, -CH<sub>3</sub>, -Cl) as alternative substitutes to control the optical response in silico [125]. Weaker electron-donating substitutions reduced the band gap to a lesser extent, e.g. -CH<sub>3</sub>. However, stronger electron-donating substitutions such as amines significantly reduced the band gap. Results demonstrated -NH<sub>2</sub>, -OH, -CH<sub>3</sub> and -Cl are the most promising and favorable substitutions. In addition, the diaminated BDC-(NH<sub>2</sub>)<sub>2</sub> linker exhibited

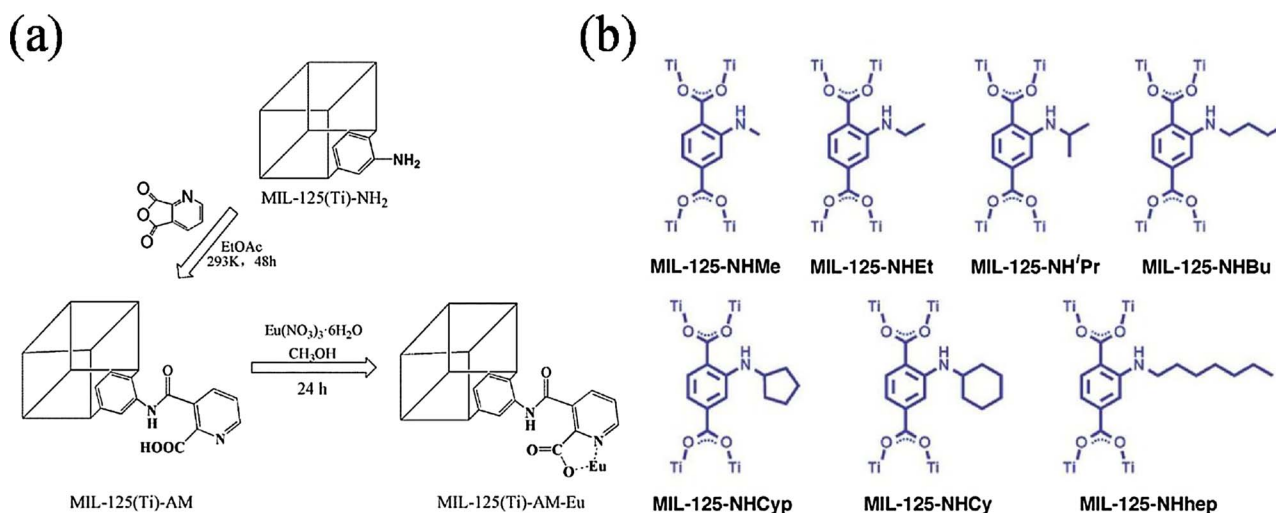


Fig. 14. Synthesis procedure of MIL-125-AM-Eu [132] (a) and N-alkyl substituted isorecticular MOFs based on MIL-125-NH<sub>2</sub> [133] (b).

the most significant red shift of 1.3 eV/950 nm with the synthesis of 10%-MIL-125-(NH<sub>2</sub>)<sub>2</sub>/90%-MIL-125-NH<sub>2</sub>. A new Europium functionalized material based on MIL-125-NH<sub>2</sub> was prepared by covalent post-synthetic modification and Eu<sup>3+</sup> coordinate load (Fig. 14a) [132]. The manufactured material performed high conversion and selectivity for photocatalytic oxidation of  $\alpha$ -phenethyl alcohol. Recently, a series of MOFs isorecticular to MIL-125-NH<sub>2</sub> were synthesized by increasing the N-alkyl substitution in MIL-125-NHR, where R varies from methyl (Me) to ethyl (Et), isopropyl (<sup>i</sup>Pr), n-butyl (Bu), cyclopentyl (Cyp), cyclohexyl (Cy), and n-heptyl (hep) (Fig. 14b) [133]. The prepared materials showed a gradual decrease in the optical band gap from 2.56 eV of MIL-125-NH<sub>2</sub> to 2.29 eV of MIL-125-NHCy, which was consistent with the increased electron density around the organic linker via inductive effects of the N-alkyl chain and the increased reaction rates and quantum yields for the photocatalytic reduction of carbon dioxide under blue LED light. In particular, MIL-125-NHCy had a smaller band gap ( $E_g = 2.3$  eV), a longer-lived excited-state ( $\tau = 68.8$  ns) and a larger apparent quantum yield ( $\Phi_{app} = 1.8\%$ ) than that of pristine MIL-125-NH<sub>2</sub> ( $E_g = 2.56$  eV,  $\tau = 12.8$  ns,  $\Phi_{app} = 0.31\%$ ). The morphologies and sizes modification of MIL-125-NH<sub>2</sub> crystal utilizing a facile surfactant for photocatalysis also has been studied. The surfactants of Pluronic P123 [134] and cetyltrimethyl ammonium bromide [135] were investigated and the modified MIL-125-NH<sub>2</sub> showed enhanced photocatalytic activity for the deoxygenation reaction [134] and RhB degradation [135].

#### 4.1.2. Combination with semiconductors

For MIL-125, the strategy by combining with semiconductor for photocatalysis is also frequently-used. The mechanism is the same as that of UiO-66. Highly photoactive g-C<sub>3</sub>N<sub>4</sub>/MIL-125 hybrids with large surface area, mesoporous heterostructures and stability were synthesized by a solvothermal strategy and the bulk g-C<sub>3</sub>N<sub>4</sub> acted as the supporter for the formation of heterostructures (Fig. 15a) [136]. The composites showed more efficient photocatalytic performance for RhB degradation that is 2.1 and 24 times as high as that of pure g-C<sub>3</sub>N<sub>4</sub> and MIL-125. The indirect dye photosensitization, Ti<sup>3+</sup>-Ti<sup>4+</sup> intervalence electron transfer and the synergistic effect between MIL-125 and g-C<sub>3</sub>N<sub>4</sub> were responsible for the enhanced photocatalytic activity. However, bulk g-C<sub>3</sub>N<sub>4</sub> suffers the predicament of limited photocatalytic activity due to low quantum yield and high recombination rate of photo-induced charge carriers [136]. The layer g-C<sub>3</sub>N<sub>4</sub> nanosheets with high specific surface area exhibit many intriguing properties compared to bulk g-C<sub>3</sub>N<sub>4</sub> [137]. On this basis, a new hybrid heterostructured MIL-125/Ag combined with g-C<sub>3</sub>N<sub>4</sub> nanosheets were prepared by Yang and co-workers in 2017 [138]. During the process, MIL-125/Ag was firstly

synthesized by a photo-reduction deposition method and then g-C<sub>3</sub>N<sub>4</sub> nanosheets were adhered onto the MIL-125/Ag composite. Ag NPs acted as an electron-conduction bridge in the interface between MIL-125 and g-C<sub>3</sub>N<sub>4</sub> nanosheets, which facilitate the direct migration of photo-induced electrons from g-C<sub>3</sub>N<sub>4</sub> to MIL-125 and retard the recombination of electron-holes. The MIL-125/Ag/g-C<sub>3</sub>N<sub>4</sub> nanocomposites showed high photocatalytic activity both for the photocatalytic reduction of nitrocompounds and the oxidation of alcohols. A latest study developed MIL-125-NH<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiPd composites by coating g-C<sub>3</sub>N<sub>4</sub> nanosheets onto MIL-125-NH<sub>2</sub> and followed by depositing Ni/Pd cocatalysts onto MIL-125-NH<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> surface [139]. Compared to the monometallic-based photocatalysts, MIL-125-NH<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>1.5</sub>Pd<sub>2.1</sub> behaved the highest photocatalytic activity for H<sub>2</sub> production rate of 8.7 mmol g<sup>-1</sup> h<sup>-1</sup>. Very recently, the Z-scheme heterojunction photocatalysts captured plenty of attention [140], owing to the high charge separation efficiency and strong redox ability. However, the construction of Z-scheme heterojunction photocatalysts based on MOFs was infrequent. Zhou and co-workers firstly combined the MIL-125-NH<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub> functionalized by benzoic acid to synthesize the g-C<sub>3</sub>N<sub>4</sub>/MIL-125-NH<sub>2</sub> Z-scheme heterostructured photocatalysts for the H<sub>2</sub> production (Fig. 15b) [141]. Benzoic acid functionalized g-C<sub>3</sub>N<sub>4</sub> participated in the coordination of Ti<sub>8</sub>O<sub>8</sub> clusters and 2-aminoterephthalic acid, and g-C<sub>3</sub>N<sub>4</sub> finally connected with MIL-125-NH<sub>2</sub> by covalent bonds. The bond acted as a mediator for the transfer of electrons from the conduction band of g-C<sub>3</sub>N<sub>4</sub> to the value band of MIL-125-NH<sub>2</sub> and meanwhile combined with the holes on MIL-125-NH<sub>2</sub>, leading to a strong redox ability.

Many other semiconductors combination with MIL-125 have been reported as well. In 2014, MIL-125@TiO<sub>2</sub> composite was synthesized by a single-step hydrothermal synthesis for the application of a depleted perovskite/TiO<sub>2</sub>-MOF heterojunction solar cell [142]. Later, a MIL-125-NH<sub>2</sub>/TiO<sub>2</sub> hybrid was synthesized to construct a sensitive photoelectrochemical sensor for the determination of the herbicide clethodim under visible-light irradiation [143]. In 2016, a novel core-shell In<sub>2</sub>S<sub>3</sub>@MIL-125 composite that MIL-125 acted as the core and three-dimensional In<sub>2</sub>S<sub>3</sub> sheets network as the shell was prepared via a facile solvothermal method for the photocatalytic degradation of tetracycline [144]. At the same year, a series of BiOBr/MIL-125-NH<sub>2</sub> composites were prepared by a co-precipitation method and the prepared composites showed an enhanced photocatalytic activity for the degradation of RhB [145]. Very recently, a potassium poly (heptazine imide) (PHIK) were incorporated into MIL-125-NH<sub>2</sub> via simply dispersing the two materials in water in virtue of the electrostatic interactions [146]. The PHIK possesses negative surface charge while MIL-125-NH<sub>2</sub> takes positive surface charge. The composites exhibited a superior



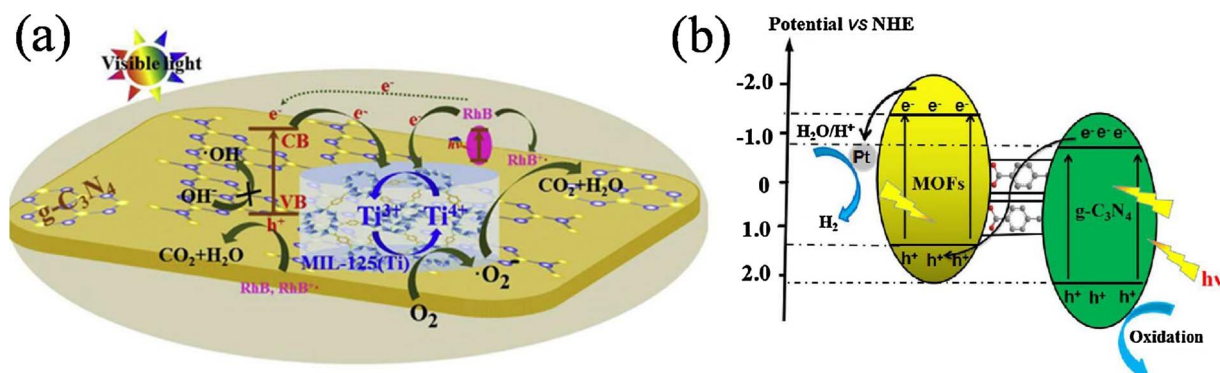


Fig. 15. The photocatalytic degradation procedure of RhB over  $g\text{-C}_3\text{N}_4/\text{MIL-125}$  hybrid [136] (a) and the  $\text{H}_2$  production through the Z-scheme heterostructured photocatalyst [141] (b).

photocatalytic activity in RhB degradation under blue light irradiation (465 nm).

#### 4.1.3. MNPs loading

The studies for MNPs loading on MIL-125 as photocatalyst are more than those of UiO-66 and the investigations mainly focus on Pt [147–150], Au [148,149], Pd [149], Ag [151–153] and Ni [154,155]. The first attempt for Pt NPs loading on MIL-125- $\text{NH}_2$  was for hydrogen production in 2012 [150]. The transferred routes of photo-induced electrons among organic linker, titanium-oxo cluster and Pt NPs have been investigated in detail. Later, Pt@MIL-125- $\text{NH}_2$  has been applied as a photocathode material for photoelectrochemical hydrogen production [147]. The Pt@MIL-125- $\text{NH}_2$  was successfully synthesized by a double solvents method, and the internal Pt NPs were smaller than 4 nm. Li and co-workers synthesized M/MIL-125- $\text{NH}_2$  ( $M = \text{Pt}$  and  $\text{Au}$ ) via a wetness impregnation method followed by a treatment with  $\text{H}_2$  flow [148]. Its photocatalytic activities were evaluated by the photocatalytic reduction of  $\text{CO}_2$  to formate. Compared with pristine MIL-125- $\text{NH}_2$ , Pt and Au loading exhibited different effects on the photocatalytic performance, where Pt/MIL-125- $\text{NH}_2$  showed an enhanced activity for photocatalytic formate formation while Au had a negative effect on the reaction. The ESR studies and DFT calculations demonstrated that the hydrogen can spillover from Pt to the bridging oxygen linked to Ti atoms, resulting in the formation of  $\text{Ti}^{3+}$  and an enhanced performance for  $\text{CO}_2$  reduction to produce formate. However, the behavior was difficult for Au/MIL-125- $\text{NH}_2$  to achieve, leading to a poor photocatalytic performance. In the preparation of MNPs/MOFs, the strong reducing and capping agents are necessary to control the morphology and size distribution of metal NPs. However, the residual organic agents are detrimental to the catalytic reaction. Thus, a facile and general method without using extra reducing and capping agents is necessary. In 2015, through a redox reaction between the reductive MIL-125 with  $\text{Ti}^{3+}$  and metal salt precursors, Pt, Au and Pd NPs were uniformly deposited onto MIL-125 without using any extra reducing or stabilizing agents (Fig. 16) [149]. The prepared M/MIL-125 ( $M = \text{Pt}$ ,  $\text{Au}$  and  $\text{Pd}$ ) showed enhanced photocatalytic activity for the selective oxidation of benzyl alcohol and  $\text{H}_2$  production compared to pure MIL-125.

Ag NPs are known as good electron sinks due to the Schottky barrier at the metal-semiconductor interface [156]. Via post-synthetic modification of MIL-125- $\text{NH}_2$  with acetylacetone (AC) vapor under nitrogen followed by the reduction of  $\text{Ag}^+$ , Ag/MIL-125-AC had a band gap of 2.09 eV and a remarkably improved photocatalytic activity for the degradation of MB under visible-light irradiation [151]. Simultaneously, Ag/MIL-125 composites with a uniform diameter of about 40 nm of Ag NPs have been prepared by a hydrothermal and photo-reduction method in 2015 [153]. GO decorated Ag/MIL-125 were also synthesized via one-pot self-assembly and photoreduction strategy [152]. The two composites were utilized for the photocatalytic degradation of RhB under visible-light irradiation. A composite of MIL-125- $\text{NH}_2$  and a molecular  $[\text{Ni}(\text{dmbpy})(2\text{-mpy})_2]$  catalyst has been prepared by

stepwise assembly of the complex in the presence of a MOF [155]. The resultant composite was evaluated by photocatalytic hydrogen production. Over the course of the composite catalyst's lifetime, different nickel (Ni) species played the leading roles and  $\text{Ni}^{2+}$  was reduced into catalytically active elemental nickel with the first efficient 1000 min. In addition, the Ni NPs-doped MIL-125- $\text{NH}_2$  was also developed for the photocatalytic aerobic oxidation of aromatic alcohols under visible-light irradiation by Fu and co-workers [154].

#### 4.1.4. Pyrolyzation

The synthesis and characterization of transition metal oxides with controlled size and shape as well as uniform dimension have drawn intensive interests due to their unique physical and chemical properties and promising applications in the fields of catalysis [157–159]. Among them, titania ( $\text{TiO}_2$ ) is a typical and practical photocatalyst due to its unique properties, economy and nontoxicity [160–162]. Nevertheless, the syntheses of  $\text{TiO}_2$  with controlled phase, shape and morphology still remain a challenge. MOFs possess highly ordered porous structures with abundant organic ligands and its metal and oxygen atoms arrange at the periodical atom level in MOFs crystals. Thus, MOFs can be completely converted into metal oxides without long-range atomic migration, which would be good candidates as sacrificial templates to give highly porous carbon or oxide materials under proper thermolysis conditions [163]. Therefore,  $\text{TiO}_2$  derived from pyrolysis of MIL-125 for photocatalysis is a typical example, though most of photocatalytic reactions were carried out under UV-light irradiation.

In 2014, a series of  $\text{TiO}_x/\text{C}$  composites were prepared by pyrolyzing MIL-125 under Ar atmosphere at 400, 600, 800 and 1000 °C, respectively [164]. Its photocatalytic performance was evaluated by the degradation of MB, and the best photocatalytic performance was achieved in MIL-125 pyrolyzed at 1000 °C due to its high surface area, reduced  $\text{Ti}_3\text{O}_5$  composition and conductive matrix.  $\text{TiO}_2$  derived from MIL-125 pyrolysis could act as a support matrix for the dispersion and stabilization of small MNPs. Khaletskaia and co-workers deposited Au NPs onto the surface of MIL-125- $\text{NH}_2$  during the solvothermal synthesis of MIL-125- $\text{NH}_2$  [165]. Consequently, Au NPs/ $\text{TiO}_2$  were fabricated through the pyrolysis of Au NPs/MIL-125- $\text{NH}_2$  under  $\text{O}_2$  atmosphere at 450 °C (Fig. 17), and the photocatalytic activity for  $\text{CO}_2$  reduction to  $\text{CH}_4$  was significantly enhanced compared to pure  $\text{TiO}_2$  and P25 under UV-light irradiation. Besides, the  $\text{TiO}_2$  from MIL-125 pyrolysis could also play a role of photoanode in the dye-sensitized solar cells [166]. The obtained  $\text{TiO}_2$  from MIL-125 pyrolyzed at 380 °C under air atmosphere possessed a large specific surface area of  $147 \text{ m}^2 \text{ g}^{-1}$  and a mean pore size of 10 nm. The overall energy conversion efficiency reached up to 7.2% when it was utilized as a photoanode material in dye-sensitized solar cells. Cake like anatase/rutile mixed phase  $\text{TiO}_2$  (A/R  $\text{TiO}_2$ ) with the size of about 500 nm was achieved from two pyrolytic section of MIL-125 under air atmosphere, first section was under 380 °C and the second was 500 °C [167], which almost reserved the intact microstructure of the MIL-125 crystal. The photocatalytic activity of A/R

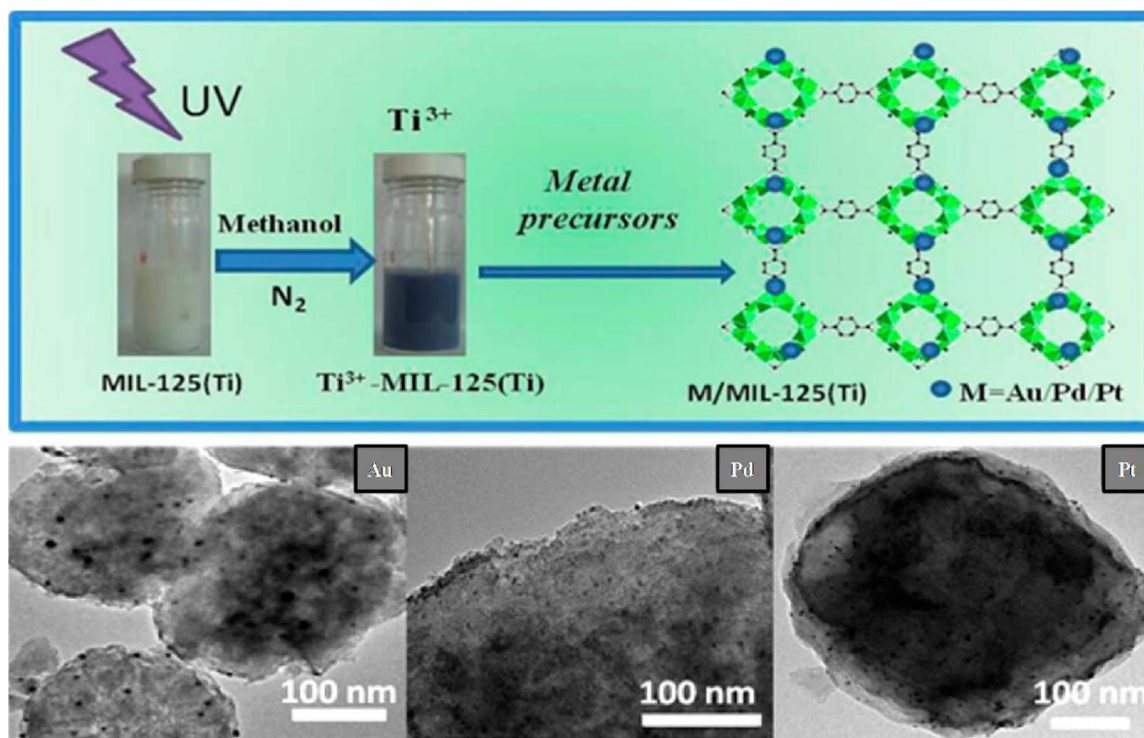


Fig. 16. Schematic presentation for the synthesis of M/MIL-125(Ti) (M = Au, Pd, Pt) composites and their TEM images [149].

TiO<sub>2</sub> for degradation of nitrobenzene was higher than that of the single anatase phase or rutile phase TiO<sub>2</sub>. Following this study, they slightly changed the second section of pyrolysis in ammonia atmosphere and synthesized cake-like A/R N-TiO<sub>2</sub> [168]. The N-doping reduced the presence of stepwise energy levels in anatase and rutile TiO<sub>2</sub> [161], leading to the enhanced photocatalytic activity to RhB degradation under visible-light irradiation.

Pyrolyzation is a specific modification strategy for limited MOFs including MIL-125, ZIF-8 and ZIF-67. The control to crystal structure and integrity of frameworks are the key factors to the synthesis of high performance metal-oxide photocatalysts. But in some time, the photocatalytic activity after pyrolyzation would be decreased to some degree owing to the obviously reduced surface area and destructive structures.

#### 4.1.5. Incorporation with other functional materials

Except the above-mentioned types of decoration of MIL-125 for photocatalysis, there are also other minority strategies to modify MIL-125, such as dye sensitization [169], decorated by RGO [170] and molecular photocatalysts encapsulation [171,172]. MIL-125-NH<sub>2</sub> has

been post-synthetically functionalized with methyl red [169]. The new material exhibited an increased absorption over a wide range of the visible spectrum, leading to the enhanced photocatalytic performance for the selective photo-oxidation of benzyl alcohol under visible-light irradiation. Up to now, examples of cooperative action between a MOF matrix and encapsulated molecular photocatalysts are very infrequent [171,172] due to the harsh terms of the choices of molecular catalysts and MOFs topology. The three conditions of the guest@MOFs composite should be satisfied: (1) photoresponsive struts for fast light-harvesting, (2) redox-active (multi) metallic nodes to allow charge-separation and accumulation of electrons, (3) an appropriate MOFs topology (i.e. large cavities connected by smaller windows) to encapsulate a molecular complex/nanocluster for productive turnover [171]. In 2015, through introducing a derivative of the well-known molecular Co-based electrocatalyst Co-dioxime-diimine (Co<sup>III</sup>Br<sub>2</sub>(L<sup>H</sup>)) into the pores of MIL-125-NH<sub>2</sub> (denoted as Co@MIL-125-NH<sub>2</sub>) following a ‘Ship-in-a-bottle’ strategy, Nasalevich and co-workers synthesized a highly active photocatalyst for the H<sub>2</sub> production from water under visible-light irradiation [171]. As shown in Fig. 18a, a direct

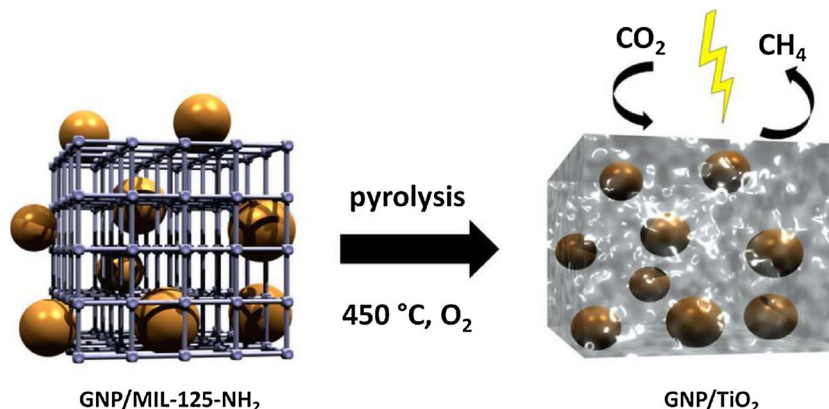


Fig. 17. Schematic diagram of the synthesis and photocatalytic reaction of GNP/TiO<sub>2</sub> [165].

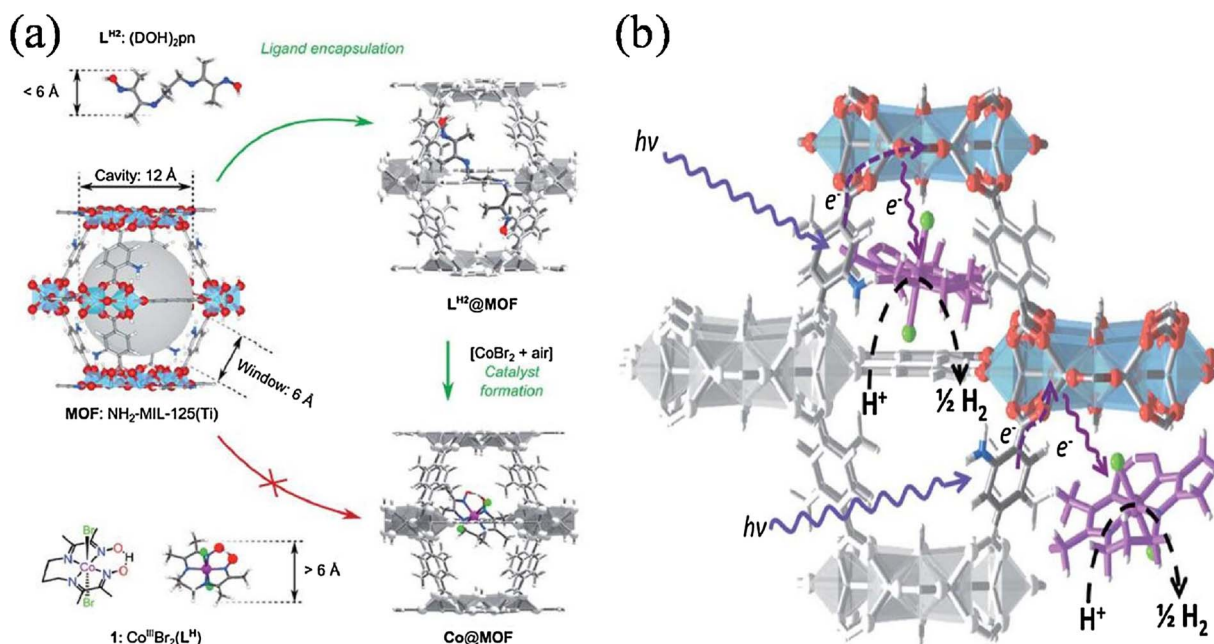


Fig. 18. 'Ship-in-a-bottle' synthetic strategy followed for assembling of Co@MOF (a), photocatalytic  $\text{H}_2$  production using a multifunctional Co@MOF photocatalyst (b) [171].

encapsulation of  $\text{Co}^{\text{III}}\text{Br}_2(\text{L}^{\text{H}})$  into MIL-125- $\text{NH}_2$  was unachievable due to the bigger size ( $> 6 \text{ \AA}$ ), which was unable to enter into the interior of MIL-125- $\text{NH}_2$  framework from the window ( $6 \text{ \AA}$ ). Therefore, the design of two-stage 'ship-in-the-bottle' strategy was needed. The flexible organic component  $(\text{DOH})_2\text{pn}(\text{L}^{\text{H}_2})$  ( $< 6 \text{ \AA}$ ) was firstly encapsulated into the framework of MIL-125- $\text{NH}_2$ , and then the  $\text{Co}^{\text{III}}\text{Br}_2(\text{L}^{\text{H}})$  was assembled after addition of  $\text{CoBr}_2$  under aerobic conditions within the large cavities of MIL-125- $\text{NH}_2$ . The band gap energy of prepared Co@MIL-125- $\text{NH}_2$  composites is 2.59 eV. When the visible light irradiated, the internal electrocatalyst  $\text{Co}^{\text{III}}\text{Br}_2(\text{L}^{\text{H}})$  could accept the photo-excited electrons from the LUMO of MIL-125- $\text{NH}_2$  and the photocatalytic  $\text{H}_2$  production happened on its surface (Fig. 18b). Introduction of the molecular Co catalytic active site led to a 20-fold enhancement in  $\text{H}_2$  production compared with the pristine MIL-125- $\text{NH}_2$ . Similarly,  $[\text{Co}^{\text{II}}(\text{TPA})\text{Cl}][\text{Cl}]$  (TPA = tris(2-pyridylmethyl)-amine) was also encapsulated into the cages of MIL-125- $\text{NH}_2$  by two-stage 'ship-in-the-bottle' strategy for visible-light-driven  $\text{H}_2$  production in 2016 [172].

Overall, MIL-125 is one of the most popular MOFs in photocatalysis due to its stability in aqueous media and both photo- and redox-active multinuclear Ti-centers. In consideration of this, MIL-125 is more suitable than UiO-66 for utilizing as photocatalyst. However, research on various decoration methods is insufficient, especially on the strategy of combination with semiconductor. Many strategies to UiO-66 modification as photocatalysts would be worthy to attempt on MIL-125. Thus, MIL-125 holds a significant potential, which is very likely to surpass that of UiO-66 in the future. The modified strategies of MIL-125 and their corresponding applications are listed in Table 3.

#### 4.2. MIL-101, MIL-100 and MIL-53

In 2005, the mesoporous chromium terephthalate MIL-101 ( $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}[\text{BDC}]_3\text{nH}_2\text{O}$ , BDC = terephthalic acid) was firstly synthesized by Ferey and co-workers and the Cr MOFs showed good resistance to air, water, popularly-used solvents and heat stability up to  $300^\circ\text{C}$  [173]. MIL-101 has two kinds of zeotype quasi-spherical cages with free internal diameters of ca. 29 and  $34 \text{ \AA}$  and microporous windows of ca. 12 and  $16 \text{ \AA}$ . It has an extremely large surface area ( $2909.85 \text{ m}^2 \text{ g}^{-1}$ ) [174] and numerous potential coordinatively unsaturated sites [175]. More importantly, MIL-101 is one of the typical MOFs with visible-light response [174,176–179], which is ascribed to the d-d spin-allowed

transition of the  $\text{Cr}^{3+}$  ( $d^5$ ) [180]. MIL-100, a Fe (III) containing MOF built up from Fe-O octahedra clusters and benzene-1,3,5-tricarboxylic acid, has been firstly prepared by Horcajada and co-workers in 2007 [181]. Due to the high thermal ( $\sim 270^\circ\text{C}$ ), photo, chemical and water stability, especially the response to visible light (band gap energy: 1.8 eV [182]) [65,181,183], MIL-100 has been selected as a representative MOF for visible-light-driven photocatalysis. MIL-53 possesses three isostructures: different metal center (Fe, Cr and Al) with the same organic linkers  $\text{H}_2\text{BDC}$  [184–186]. All of them are chemical, thermal stability and low toxicity. The onset of the main absorption edge of MIL-53(Fe), MIL-53(Cr) and MIL-53(Al) was 455, 395 and 320 nm, corresponding to the band gaps of 2.72, 3.20 and 3.87 eV, respectively [51]. Among them, MIL-53(Fe) were aroused extremely interest, since it is visible-light-response and iron is an earth-abundant element. MIL-53(Fe) is a three-dimensional porous solids composed of infinite  $\text{FeO}_4(\text{OH})_2$  clusters connected by  $\text{H}_2\text{BDC}$  ligand [187]. The visible-light responsive property implies that MIL-101, MIL-100 and MIL-53 can act as a visible-light active photosensitizer, which determines that most photocatalytic reactions based on them can be carried out under visible-light irradiation.

The studies of MILs utilizing as photocatalysts are mainly concentrated on: decoration of linker [188,189], combination with semiconductors [174,176,178,179,182,190–200], MNPs loading [177,196,201–208], decoration by RGO and GR [209–212], and incorporation with other functional materials [213,214].

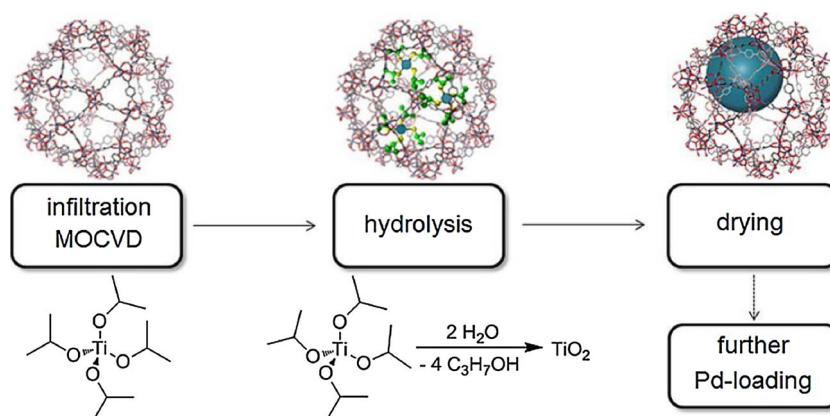
##### 4.2.1. Decoration of linker

The studies of linker decoration mainly focused on MIL-53. Although MIL-53(Fe) can absorb visible light, the photocatalytic activity could still be improved to a certain degree via the linker decorated by amino. Shi and co-workers confirmed that the amine-functionalized MIL-53(Fe)- $\text{NH}_2$  exhibited an enhanced visible-light absorption and photocatalytic activity for Cr(VI) photocatalytic reduction compared to MIL-53(Fe). An and co-workers synthesized two Al based MOFs (MIL-53(Al) and MIL-53(Al)- $\text{NH}_2$ ) and investigated their photoelectrical, photophysical and photocatalytic properties in oxygen evolution from water [189]. According to the results of theoretical calculation, steady state and time resolved fluorescence spectra, a new photocatalytic mechanism based on electron tunneling was proposed, which was different from the LMCT theory.



**Table 3**  
Modified strategies of MIL-125 and their corresponding applications.

| Strategies                      | details                         | MOF                         | Applications                                  | Light source | Ref.      |
|---------------------------------|---------------------------------|-----------------------------|---|--------------|-----------|
| Decoration of linker            | -NH <sub>2</sub>                | MIL-125                     | CO <sub>2</sub> , Cr(VI) reduction            | Visible      | [45,129]  |
|                                 | -NH <sub>2</sub>                | MIL-125                     | Amines oxidation                              | Visible      | [126]     |
|                                 | -NH <sub>2</sub>                | MIL-125                     | Alcohols oxidation                            | Visible      | [127]     |
|                                 | -NH <sub>2</sub>                | MIL-125                     | N-hydroxy-carbamates                          | UV-vis       | [130]     |
|                                 | -NH <sub>2</sub>                | MIL-125                     | PCVG  | UV           | [131]     |
|                                 | -AM-Eu                          | MIL-125-NH <sub>2</sub>     | Alcohols oxidation                            | UV-vis       | [132]     |
| Combination with semiconductors | NHMe, NH <sub>2</sub> Et, NHPr  | MIL-125-NH <sub>2</sub>     | CO <sub>2</sub> reduction                     | Visible      | [133]     |
|                                 | g-C <sub>3</sub> N <sub>4</sub> | MIL-125                     | RhB degradation                               | Visible      | [136]     |
|                                 | g-C <sub>3</sub> N <sub>4</sub> | Ag/MIL-125                  | Nitrobenzene reduction and alcohols oxidation | Visible      | [138]     |
|                                 | g-C <sub>3</sub> N <sub>4</sub> | NiPd/MIL-125                | H <sub>2</sub> production                     | Visible      | [139]     |
|                                 | CFB                             | MIL-125-NH <sub>2</sub>     | H <sub>2</sub> production                     | Visible      | [141]     |
|                                 | In <sub>2</sub> S <sub>3</sub>  | MIL-125                     | Tetracycline degradation                      | Visible      | [144]     |
|                                 | BiOBr                           | MIL-125-NH <sub>2</sub>     | RhB degradation                               | Visible      | [145]     |
|                                 | PHIK                            | MIL-125-NH <sub>2</sub>     | RhB degradation                               | Visible      | [146]     |
|                                 | TiO <sub>2</sub>                | MIL-125                     | Solar cell                                    | Solar light  | [142]     |
|                                 | TiO <sub>2</sub>                | MIL-125-NH <sub>2</sub>     | Photoelectrochemical sensor                   | Visible      | [143]     |
| MNPs loading                    | Pt, Au                          | MIL-125                     | H <sub>2</sub> , formate production           | Visible      | [148]     |
|                                 | Au, Pd, Pt                      | MIL-125                     | H <sub>2</sub> production, alcohols oxidation | UV-vis       | [149]     |
|                                 | Ag                              | MIL-125                     | RhB degradation                               | Visible      | [153]     |
|                                 | Ag                              | RGO/MIL-125                 | RhB degradation                               | Visible      | [152]     |
|                                 | Ni                              | MIL-125-NH <sub>2</sub>     | H <sub>2</sub> production                     | UV           | [155]     |
|                                 | Ag                              | MIL-125-AC                  | MB degradation                                | Visible      | [151]     |
|                                 | Pt                              | MIL-125-NH <sub>2</sub>     | Photocathode, H <sub>2</sub> production       | Visible      | [147,150] |
|                                 | Ni                              | MIL-125-NH <sub>2</sub>     | Alcohols oxidation                            | Visible      | [154]     |
|                                 | TiO <sub>2</sub>                | MIL-125                     | Photoanode                                    | UV-vis       | [166]     |
|                                 | TiO <sub>2</sub> /C             | MIL-125                     | MB degradation                                | UV           | [164]     |
| Pyrolyzation                    | GNP/TiO <sub>2</sub>            | GNP/MIL-125-NH <sub>2</sub> | CO <sub>2</sub> reduction                     | UV           | [165]     |
|                                 | A/R TiO <sub>2</sub>            | MIL-125                     | Nitrobenzene degradation                      | UV           | [167]     |
|                                 | A/R N-TiO <sub>2</sub>          | MIL-125                     | RhB degradation                               | Visible      | [168]     |
|                                 |                                 |                             |   |              |           |



**Fig. 19.** Preparation of TiO<sub>2</sub>@MIL-101 by MOCVD [192].

#### 4.2.2. Combination with semiconductors

The earliest semiconductor combining with MIL-101 and MIL-100 is CdS. In 2013, He and co-workers demonstrated that embedding of CdS NPs (2–3 nm) on MIL-101 could significantly increase the photocatalytic efficiency of CdS for the visible-light-promoted hydrogen production when using Pt as co-catalyst [174]. The effective dispersion of CdS particles and the sensitization of CdS by MIL-101 were responsible for the enhanced photocatalytic activity. Besides, they demonstrated that the photo-induced electrons were transferred from the CB of MIL-101 to that of CdS because the lower CB potential of MIL-101. Jiang and co-workers introduced polyoxo-titanium clusters into the CdS/MIL-101 system that resulted in a highly efficient visible-light-range H<sub>2</sub>-evolution photocatalysts [191]. The introduced polyoxo-titanium acted a mediator to transfer the photo-induced electrons between CdS and MIL-101. It remains controversial that the transfer direction of electrons was from CB of CdS to that of MIL-101 in this report. Similarly, MIL-100 combined with CdS was synthesized via a solvothermal method by Ke and co-workers in 2015 [182]. The prepared CdS-MIL-

100 nanocomposites exhibited enhanced visible-light photocatalytic activity for the selective oxidation of benzyl alcohol to benzaldehyde. Meantime, He and co-workers made CdS NPs be dispersed and embedded on MIL-100 for photocatalytic degradation of nitrite ions through a disproportionation in a neutral aqueous solution without any sacrificial reagents [195]. The photo-induced electrons reduced NO<sub>2</sub><sup>−</sup> to yield the NH<sub>4</sub><sup>+</sup> and the holes oxidized NO<sub>2</sub><sup>−</sup> to produce NO<sub>3</sub><sup>−</sup> at the same time. When 20 wt% of CdS was embedded on MIL-100, the degradation yield was five folds to bare CdS. The enhancement in photocatalytic activities was ascribed to photosensitization and supporting of MIL-100 scaffold. Very recently, a Co-Ni sulfide Co<sub>2</sub>Ni<sub>2</sub>S<sub>4</sub>@MIL-101 exhibited an outstanding photocatalytic activity for H<sub>2</sub> production (882.7 μmol in 120 min) after sensitized by Eosin Y under visible-light irradiation at pH 9 [194]. The high photocatalytic efficiency was ascribed to the low ΔG<sub>H</sub> over Co<sub>2</sub>Ni<sub>2</sub>S<sub>4</sub>, stable reaction intermediate during hydrogen formation and better photoelectrochemical properties.

Due to the property of visible-light response, MIL-101 and MIL-100 even could incorporate with semiconductor with no visible-light

absorption, e.g.  $\text{TiO}_2$  [178,179,190,192,199]. In 2015, the controlled incorporation of nanoscale palladium and titanium dioxide inside MIL-101 was accomplished by metal-organic chemical vapor deposition (MOCVD) (Fig. 19) [192]. The Ti-precursor  $[\text{Ti}(\text{O}-i\text{P})_4]$  was infiltrated into MIL-101 by MOCVD and thermally decomposed to titania under water atmosphere. Subsequently, the same gas-phase loading of  $[(\text{C}_5\text{H}_5)_2\text{Pd}(\text{C}_3\text{H}_5)]$  and reduction by hydrogen gave rise to  $\text{Pd}/\text{TiO}_2@\text{MIL-101}$  composites. The prepared  $\text{Pd}/\text{TiO}_2@\text{MIL-101}$  showed efficient photocatalytic activity in hydrogenation and dehydrogenation. Subsequently, they prepared the MIL-101-core-Au/anatase-shell photocatalyst for visible-light-driven degradation of dyes and the antibiotic ciprofloxacin from wastewater [179]. In order to further improve the absorption of visible light by MIL-101- $\text{NH}_2$ , Li and co-workers modified it with salicylaldehyde and made  $\text{TiO}_2$  be encapsulated [178]. The conjugated linker was elongated and the resulting framework showed enhanced absorption of visible light. The MB degradation was dramatically enhanced from 30% of  $\text{TiO}_2@\text{MIL-101-NH}_2$  to 86% of  $\text{TiO}_2@\text{Salicylaldehyde-MIL-101-NH}_2$ .  $\text{TiO}_2@\text{MIL-101}$  core-shell composites were also fabricated for the adsorption and photocatalytic degradation of MO by Chang and co-workers [190]. Designing and building hierarchically porous structures through assembling 2D  $\text{TiO}_2\text{NS}$  with MOFs was verified as an ideal solution to create a large number of functional interfaces [215]. Based on this, a hierarchical sandwich-like  $\text{TiO}_2\text{NS}@\text{MIL-100}$  heterostructure was developed through a self-assembled method by incorporating MIL-100 into  $\text{TiO}_2\text{NS}$  [199]. The nanocomposites exhibited good adsorption capacity and enhanced visible-light photocatalytic degradation of MB due to the porous MIL-100 loading and the sandwich-like heterostructure that provides a platform for high-speed interfacial photogenerated charges transfer.  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , a typical Keggin-type polyoxometalates, was encapsulated in the pores of MIL-100 for the selective oxidation of alcohols and the reduction of heavy metal ions  $\text{Cr}(\text{VI})$  under visible-light irradiation by Liang and co-workers [216]. They found that  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  acted as the major photocatalyst in the selective oxidation system while MIL-100 played the key role in the  $\text{Cr}(\text{VI})$  reduction process.

$\text{N-K}_2\text{Ti}_4\text{O}_9$  [176] was also been investigated to incorporate with MIL-101 for MB degradation under visible-light irradiation. MIL-100 grown on  $\text{g-C}_3\text{N}_4$  nanosheets for the photocatalytic degradation of RhB was reported by Hong and co-workers [197]. Bismuth-based semiconductors such as  $\text{BiWO}_4$  and  $\text{Bi}_2\text{MoO}_6$  were successfully incorporated into MIL-100 for the visible-light photocatalytic degradation salicylic acid [198] and RhB [200], respectively. Zheng and co-workers proved that p-n junction formed by n-type semiconductor  $\text{BiWO}_4$  and p-type MIL-100 could facilitate the photogenerated charge separation [198].

#### 4.2.3. MNPs loading

MNPs loading on MILs is the other major direction for utilizing MILs as photocatalysts. Pt NPs were firstly incorporated into MIL-101- $\text{NH}_2$  for the visible-light-driven  $\text{H}_2$  production with RhB sensitization in 2014 [201]. The porous MIL-101- $\text{NH}_2$  not only served as electric conductors to promote the electron transfer, but also acted as photo-electron generators through LMCT mechanism.  $\text{Ni}/\text{NiO}_x$  particles instead of noble metals were in situ photodeposited on MIL-101 for boosting  $\text{H}_2$  generation with Erythrosin B dye sensitization under visible-light irradiation [202].  $\text{Pd}/\text{MIL-101}/\text{rGO}$  was fabricated for degradation of two triphenylmethane dyes, brilliant green and acid fuchsin [203].

Similar to the preparation of  $\text{Ag}/\text{AgCl}@\text{ZIF-8}$  [217–219], Gao and co-workers synthesized  $\text{Ag}/\text{AgCl}@\text{MIL-101}$  hetero-junction photocatalyst via a vapor diffusion-photoreduction process [177]. The photocatalytic activity was evaluated for the degradation of RhB under visible-light irradiation. However, most of the  $\text{Ag}/\text{AgCl}$  stuck on the external surface of the MIL-101 with large sizes of 200–500 nm due to the high speed reaction between  $\text{Ag}^+$  and  $\text{Cl}^-$  ions. To solve this problem, Yan and co-workers introduced a Ag monosubstituted polyoxometalate (POM),  $\text{K}_6[\alpha\text{-AgPW}_{11}\text{O}_{39}]$ , into MIL-101(Al)- $\text{NH}_2$  through an incipient wetness impregnation method and subsequent photo-

reduction under UV irradiation to obtain  $\text{Ag}/\text{POM-AgCl}@\text{MIL-101(Al)-NH}_2$  composite [205]. Mono-vacant POMs could coordinate with  $\text{Ag}^+$  ions, which may control the growth of  $\text{Ag}/\text{AgCl}$  nanocrystals. The as-obtained  $\text{Ag}/\text{POM-AgCl}$  composite NPs possessed an average particle size of 3.2 nm and the  $\text{Ag}/\text{POM-AgCl}@\text{MIL-101(Al)-NH}_2$  showed higher photocatalytic activity for RhB degradation than that of  $\text{Ag}/\text{AgCl}@\text{MIL-101(Al)-NH}_2$ . PNPMOF was self-assembled by a polyoxometalate (POM), Pt NPs and MIL-53(Al)- $\text{NH}_2$ , which displayed enhanced activity for visible-light-driven catalytic  $\text{H}_2$  production [220].

The alloyed catalysts could regulate electronic structures and enhance catalytic activity [221]. A highly efficient photocatalyst  $\text{NiMo}@\text{MIL-101}$  for the  $\text{H}_2$  production was fabricated by the double solvents method according to the advanced DFT and frontier molecular orbital theory calculation analysis [206]. Compared with  $\text{Ni}@\text{MIL-101}$  and  $\text{Mo}@\text{MIL-101}$ , the resulting  $\text{NiMo}@\text{MIL-101}$  showed an excellent photocatalytic performance ( $740.2 \mu\text{mol h}^{-1}$  for  $\text{H}_2$  production), stability and highly apparent quantum efficiency (75.7%) under 520 nm-light illumination at pH 7. They also demonstrated that the lower  $\Delta G_{\text{H}}$  of  $\text{Ni-Mo}(\text{MoNi}_4)$  alloy nanoclusters led to the higher  $\text{H}_2$  production activity. To sensitize Pd active sites and boost their intrinsic activity of Pd under visible-light irradiation, constructing PdAu bimetal hetero-structures was a feasible way because of the visible-light absorption and higher electronegativity of Au. Wen and co-workers fabricated  $\text{Au}/\text{Pd-MIL-101}$  photocatalysts for hydrolysis of ammonia borane and Suzuki-Miyaura coupling reaction under visible-light irradiation [204].

Liang and co-workers fabricated  $\text{M}@\text{MIL-100}$  ( $\text{M} = \text{Pd}, \text{Pt}, \text{Au}$ ) via a alcohol reduction approach for the visible-light photocatalytic degradation of three typical pharmaceutical and personal care products (PPCPs), theophylline, ibuprofen and bisphenol A [196]. The photocatalytic activities closely depended on the different types and contents of metal. The  $1\%\text{Pd}@\text{MIL-100}$  exhibited the relatively high photocatalytic activity. In addition, the addition of  $\text{H}_2\text{O}_2$  and pH value also influenced the photocatalytic reaction. Active species trapping experiments with different radical scavengers revealed that the photo-induced electrons and  $\cdot\text{OH}$  played major roles towards the degradation of PPCPs (Fig. 20). A photochemical route to synthesized  $\text{M}@\text{MIL-100}$  ( $\text{M} = \text{Pd}, \text{Pt}$ , or  $\text{Au}$ ) was developed for the photocatalytic degradation of MO and the reduction of  $\text{Cr}(\text{VI})$  in water under visible-light irradiation [207]. In this photocatalytic system,  $\text{Pt}@\text{MIL-100}$  with an average Pt particle size of 2 nm showed the highest photoactivity. Following this research line, Wang and co-workers developed a double-solvent impregnation way combined with a photoreduction process to prepare  $\text{Pd}@\text{MIL-100}$  with 1.7 nm average size of Pd NPs confined inside the cavity of MIL-100 [208]. The resultant  $\text{Pd}@\text{MIL-100}$  exhibited much higher photocatalytic activity in light-induced *N*-alkylation of amines with alcohols compared to that of Pd NPs with size of 6–12 nm loading on the external surface of MIL-100. The efficient coupling of photocatalytic dehydrogenation and Pd-based hydrogenation were responsible for the enhanced photocatalytic activity.

#### 4.2.4. Decoration by GR or RGO

The reports of MIL-53 combining with graphene are intensive, including graphene (GR) and reduced graphene oxide (RGO). In 2015, Zhang and co-workers firstly fabricated GR hybridized MIL-53(Fe) microrods through a one-pot solvothermal method [210]. GR was derived from the reduction of GO during the solvothermal process. The GR/MIL-53 systems showed significantly higher photocatalytic activity for RhB degradation than that of bare MIL-53 under visible-light irradiation in the presence of  $\text{H}_2\text{O}_2$  (Fig. 21). To seek a more efficient preparation method, MIL-53(Fe)-RGO was constructed by electrostatic self-assembly between negatively charged GO and positively charged MIL-53(Fe), followed by a solvothermal reduction of GO to RGO [209]. Compared with direct synthesis of MIL-53(Fe)-RGO via one-pot solvothermal approach, electrostatic self-assembly synthesized MIL-53(Fe)-RGO exhibited improved photocatalytic activity. In addition, MIL-53(Fe)-RGO nanocomposites were proven to be a bifunctional

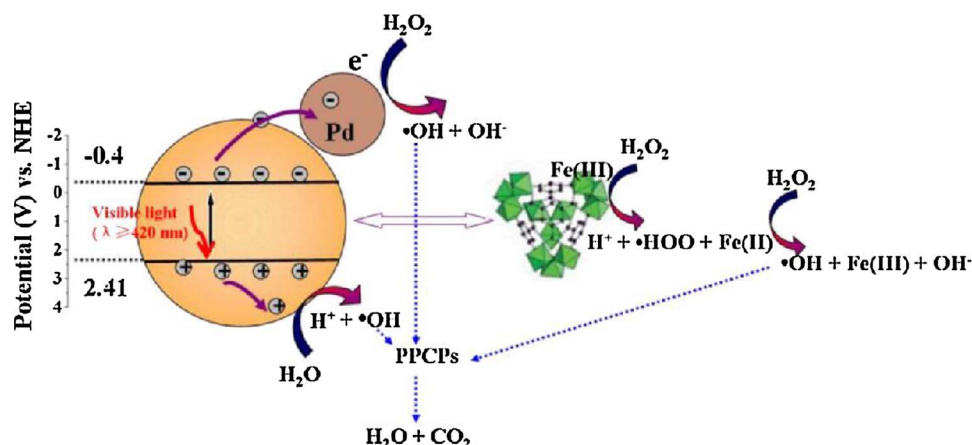


Fig. 20. Mechanism for the photocatalytic degradation of PPCPs over Pd@MIL-100(Fe) under visible-light irradiation [196].

photocatalyst with good activity in the mixed systems (Cr(VI)/dyes) under visible-light irradiation, which was similar to their previous reports [62,95]. A series of MIL-53(Fe)-GR were also synthesized for the photocatalytic selective oxidation of alcohols to the corresponding aldehydes or ketones and the selectivity could reach 99% [211]. Recently, MIL-53(Al)-NH<sub>2</sub> nanocrystals were anchored on the surface of RGO hollow spheres for photocatalytic degradation of MB [212].

#### 4.2.5. Incorporation with other functional materials

Recycling test is a very important index for catalysts in the practical applications. Compared to the conventional photocatalysts, the magnetic photocatalyst is green, cheap and more suitable for large scale industrial applications. Fe<sub>3</sub>O<sub>4</sub> NPs possess good magnetic properties and low toxicity to the environment [222], offering facile recyclability and accessibility as catalysts. However, Fe<sub>3</sub>O<sub>4</sub> is highly susceptible to photodissolution [214]. Thus, the core-shell structures with Fe<sub>3</sub>O<sub>4</sub> as the core were feasible for photocatalysis [213,214]. The magnetic Fe<sub>3</sub>O<sub>4</sub>@MIL-100 core-shell microsphere was firstly fabricated by Zhang and co-workers in 2013 [213]. The photocatalytic activity for MB was much higher than that of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> addition not only under UV–vis light but also under visible-light irradiation. Zhao and co-workers investigated the effect of H<sub>2</sub>O<sub>2</sub> addition and the thickness of MIL-100 shell to the photocatalytic degradation of MB in detail [214]. As shown in Fig. 22, H<sub>2</sub>O<sub>2</sub> acted a photo-induced electrons acceptor and the holes could transfer to Fe<sub>3</sub>O<sub>4</sub> core that the efficiency depended on the thickness of MIL-100 shell. The optimal shell thickness was about 50 nm, corresponding to the highest photocatalytic activity.

Many other approaches to improve the photocatalytic activity of MILs were carried out as well. Polyoxometalate [Co

(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> incorporating in MIL-101 was studied for the water oxidation [193], showing that the effect of the polyoxometalate was for collecting and transferring electrons. After composited with anionic resin (Amberlite IRA 200) and cationic resin (Amberlite IRA 900), two types of MIL-53(Fe) equipped with negative and positive charge (AMIL-53 and DMIL-53) were synthesized respectively [223]. AMIL-53 and DMIL-53 showed reversed photocatalytic degradation to cationic and anionic dyes under visible-light irradiation. However, very few attention has been concentrated on the development of NIR-responsive MOF photocatalysts. Recently, NaYF<sub>4</sub>:Yb,Tm/MIL-53(Fe) photocatalysts with a uniform core-shell structure have been synthesized through surface modification of the upconversion NPs and sequential coating of PVP polymer [224]. The prepared photocatalysts exhibited an enhanced activity for the degradation of RhB, MB and phenol under solar spectrum due to their response to the NIR light. A magnetic MIL-53(Fe) (MAG-MIL) has been prepared by an in-situ ethylenediamine-assisted solvothermal method [225]. The well dispersed γ-Fe<sub>2</sub>O<sub>3</sub> NPs embedded in the MAG-MIL framework led to a red shift of the light absorption edge and showed good photocatalytic activity for the degradation of MB.

In summary, MILs hold a great potential application for photocatalysis under solar light due to their wide absorption in visible-light region. The modified strategies abound as to MILs, but the effect or purpose of a single strategy to them is limited, for instance, the modified methods to MIL-101 mainly focus on combination with semiconductor and MNPs loading, whereas other modification strategies referring to that of other MOFs (e.g. UiO-66, MIL-125 and ZIF-8) have not been carried out. Therefore, the photocatalytic reactions over various MILs remain at the infant stage and numerous modification

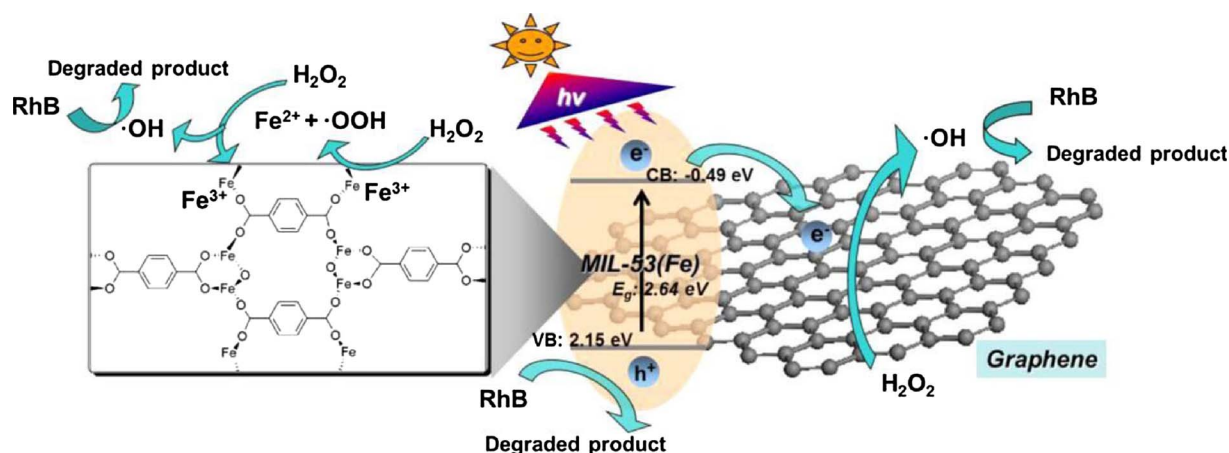


Fig. 21. Photocatalytic process of graphene/MIL-53(Fe) composite in the presence of H<sub>2</sub>O<sub>2</sub> [210].



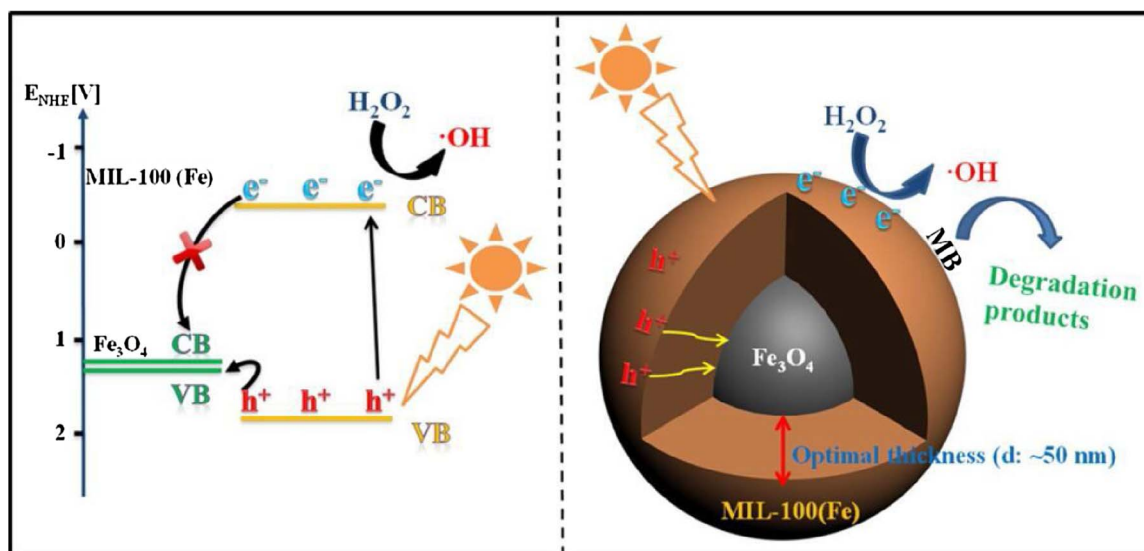


Fig. 22. The mechanism of photocatalytic degradation of MB over  $\text{Fe}_3\text{O}_4/\text{MIL-100}$  [214].

**Table 4**  
Modified strategies of MIL-101, MIL-100 and MIL-53 and their corresponding applications.

| Strategies                      | details                                 | MOF                           | Applications  | Light source | Ref.  |
|---------------------------------|---|-------------------------------|---|--------------|-------|
| Decoration of linker            | $-\text{NH}_2$                          | MIL-53(Fe)                    | Cr(VI) reduction  | Visible      | [188] |
|                                 | $-\text{NH}_2$                          | MIL-53(Al)                    | $\text{O}_2$ production                                     | UV-vis       | [189] |
| Combination with semiconductors | CdS                                     | MIL-101                       | $\text{H}_2$ production                                     | Visible      | [174] |
|                                 | $\text{N-K}_2\text{Ti}_4\text{O}_9$     | MIL-101                       | RhB degradation   | UV-vis       | [176] |
|                                 | CdS                                     | PTC/MIL-101                   | $\text{H}_2$ production                                     | Visible      | [191] |
|                                 | Salicylaldehyde/M IL-101- $\text{NH}_2$ |                               | MB degradation  | Visible      | [178] |
|                                 | $\text{TiO}_2$                          | MIL-101                       | MO degradation  | UV           | [190] |
|                                 | $\text{TiO}_2$                          | Au/MIL-101                    | $\text{H}_2$ production, antibiotics degradation            | Visible      | [179] |
|                                 | $\text{TiO}_2$                          | Pd/MIL-101                    | Hydrogenation and dehydrogenation                           | UV           | [192] |
|                                 | CdS                                     | MIL-100                       | Nitride degradation   | UV-vis       | [195] |
|                                 | CdS                                     | MIL-100                       | Alcohols oxidation  | Visible      | [182] |
|                                 | $\text{g-C}_3\text{N}_4$                | MIL-100                       | RhB degradation   | Visible      | [197] |
|                                 | $\text{BiWO}_4$                         | MIL-100                       | Salicylic acid degradation                                  | Visible      | [198] |
|                                 | $\text{Bi}_2\text{MoO}_6$               | MIL-100                       | RhB degradation   | Visible      | [200] |
|                                 | $\text{TiO}_2$                          | MIL-100                       | MB degradation  | Visible      | [199] |
|                                 | $\text{g-C}_3\text{N}_4$                | MIL-53(Al)                    | RhB degradation   | UV-vis       | [46]  |
| MNPs loading                    | Pt                                      | MIL-101- $\text{NH}_2$        | $\text{H}_2$ production                                     | Visible      | [201] |
|                                 | Ni                                      | $\text{NiO}_x/\text{MIL-101}$ | $\text{H}_2$ production                                     | Visible      | [202] |
|                                 | Pd                                      | RGO/MIL-101                   | Triphenylmethane dyes degradation                           | Visible      | [203] |
|                                 | Ag                                      | $\text{AgCl}/\text{MIL-101}$  | RhB degradation   | Visible      | [177] |
|                                 | AuPd                                    | MIL-101- $\text{NH}_2$        | Ammonia borane hydrolysis, Suzuki-Miyaura coupling reaction | Visible      | [204] |
|                                 | NiMo                                    | MIL-101                       | $\text{H}_2$ production                                     | Visible      | [206] |
|                                 | Au, Pd, Pt                              | MIL-100                       | MO degradation, Cr(VI) reduction                            | Visible      | [207] |
|                                 | Pd                                      | MIL-100                       | PPCP degradation  | Visible      | [196] |
|                                 | Pd                                      | MIL-100                       | Amines N-alkylation   | Visible      | [208] |
| Decoration by RGO and GR        | RGO                                     | MIL-53(Fe)                    | Cr(VI) reduction, dyes degradation                          | Visible      | [209] |
|                                 | RGO                                     | MIL-53(Al)- $\text{NH}_2$     | MB degradation  | UV-vis       | [212] |
|                                 | GR                                      | MIL-53(Fe)                    | RhB degradation   | Visible      | [210] |
|                                 | GR                                      | MIL-53(Fe)                    | Alcohols oxidation  | Visible      | [211] |

methods deserve to be attempted. The modified strategies of MIL-101, MIL-100 and MIL-53 and their corresponding applications are summarized in Table 4.

## 5. ZIFs

As one of the most typical MOF materials, zeolitic imidazolate frameworks (ZIFs), constructed by the tetrahedrally coordinated divalent cations ( $\text{Zn}^{2+}$  or  $\text{Co}^{2+}$ ) and imidazolate linkers, showed their capabilities in various fields [27,226–232]. Compared with the other MOFs, ZIFs not only have good thermal/chemical stability and water tolerance, but also possess tunable zeotype topologies and easy synthetic process to achieve uniform structures. Among them, ZIF-8(Zn)

and ZIF-67(Co) are two typical ZIFs utilized for photocatalyst, especially ZIF-8. However, the large band gap energy (5.1 eV) and the fixed organic linkers limit its photocatalytic activity of ZIF-8 under visible light. On the contrary, ZIF-67 has a low band gap ( $E_g = 1.98$  eV) and multiple absorption bands in the UV-vis-near IR region [72,233]. The studies about ZIF-8 for photocatalysis are much more than that of ZIF-67, probably because the easy-controlled synthesis and large researched space of ZIF-8 relatively.

### 5.1. Partial substitution of metal center

The linker of ZIFs is imidazolate, which is comparatively difficult to modify. Thus, the modifications at the molecule level of ZIFs were

concentrated on the metal center partial substitution. Early in 2012, a Cu doping strategy was applied to tune the gas sorption and photocatalytic properties of ZIF-67 [233]. Results demonstrated that Cu substituted ZIF-67 showed high  $H_2$  and  $CO_2$  uptake capacities and highly efficient degradation of MO under visible-light irradiation. Later, the active Ni metal was introduced into the metal center of ZIF-8 via a one-pot mechanochemical method under liquid assisted grinding conditions [234]. This Ni-substituted ZIF-8 adopted topology of ZIF-8 with Ni partially substituting the  $ZnN_4$  in the backbone. The samples with photoactive Ni centers and open channels exhibited outstanding photocatalytic activity for the degradation of MB under visible light.

## 5.2. Combination with semiconductors

For ZIF-8, combination with semiconductors always realized over a designed route and ZIF-8 was growing on the surface of semiconductor with a diversity of morphologies in most cases. Liu and co-workers firstly found that ZIF-8 could effectively adsorb  $CO_2$  dissolved in water and constructed a  $Zn_2GeO_4$ /ZIF-8 nanocomposite for the photocatalytic conversion of  $CO_2$  into liquid  $CH_3OH$  fuel [232]. The composites were prepared by growing ZIF-8 NPs on  $Zn_2GeO_4$  nanorods. The prepared  $Zn_2GeO_4$ /ZIF-8 hybrid nanorods with 25 wt% ZIF-8 contents exhibited 3.8 times  $CO_2$  adsorption capacity as high as that of bare  $Zn_2GeO_4$  nanorods and 62% enhancement in the photocatalytic conversion rate. Core-shell  $ZnO$ @ZIF-8 nanospheres were synthesized by a self-template method [235], where  $ZnO$  not only acted as the template but also supplied  $Zn(II)$  for the composition of ZIF-8. The photocatalytic degradation of MB was dominated by the outer ZIF-8 shell for the molecule size of MB is larger than the pore aperture of ZIF-8. Similarly, utilizing the molecule size selectivity of ZIF-8 shell, Wang and co-workers adopted the same method to construct the  $ZnO$ @ZIF-8 heterostructures for the selective reduction of  $Cr(VI)$  between  $Cr(VI)$  and MB [236] under UV-light irradiation (Fig. 23). The photoreaction active sites were located on  $ZnO$  sphere where only  $CrO_4^{2-}$  could go through the aperture of the ZIF-8 frameworks. During the synthesis process of  $ZnO$ @ZIF-8 heterostructures, they found that the concentration of organic ligand 2-methylimidazole was crucial for the preparation of core-shell heterostructures by remarkably influencing the balance between the rate of  $ZnO$  dissolution and the rate of  $Zn^{2+}$  coordination. Subsequent work has also been carried out based on  $ZnO$ /ZIF-8 composites for photocatalytic degradation of organic dyes [237].

In order to study the effect of the interfacial reaction between semiconductors and MOFs, ZIF-8 was assembled homogeneously on the surface of electrostatic spinning  $TiO_2$  nanofibers and formed a N–Ti–O bond under sonochemical treatment [215] without surfactants or

additives (Fig. 24). The newly formed chemical bond between  $TiO_2$  and ZIF-8 highly promoted the thermal stability, crystallinity and photocatalytic activity in RhB photocatalytic degradation compared to commercial P25. Three factors account for the enhanced photoactivity: (1) More light would be harnessed by the outer ZIF-8 shell with light penetration and scattering properties, (2) ZIF-8 played a role of co-catalyst together with  $TiO_2$  and (3) chemical-bonds of N–Ti–O suppressed the recombination of photo-excited electron-hole pairs. In 2017, ZIF-8 NPs were deposited on the surfaces of mesoporous  $TiO_2$  nanobeads for the photocatalytic reduction of  $Cr(VI)$  [238]. The enhanced photocatalytic activity was ascribed to the strong  $Cr(VI)$  adsorption property of ZIF-8 as well as more efficient charge transfer compared to pristine  $TiO_2$  beads. Similarly, ZIF-8 nanoclusters were grown on the  $g-C_3N_4$  nanotubes as well for the  $CO_2$  photocatalytic reduction [239]. The yield of methanol over  $g-C_3N_4$ /ZIF-8 composite reached to  $0.75 \mu mol h^{-1} g^{-1}$  that was about 3 times than that of pure  $g-C_3N_4$ . The excellent  $CO_2$  adsorption by grafting additional ZIF-8 nanoclusters was responsible for the enhanced photocatalytic activity. However, the conductivity of most MOFs is not good enough, which limited the charge transfer to a certain degree. Thus, the loading amount of MOFs is a crucial parameter for photocatalysis. The nanosheets of  $g-C_3N_4$  were also anchored onto ZIF-8 microstructures and a highly stable micro-meso porous architecture was formed for the adsorption and photocatalytic degradation of tetracycline [240]. To integrate dual photothermal- and catalytic-functionality, a core-shell hierarchical  $Cu_7S_4$  nano-heater@ZIF-8 heterostructures were prepared for the cyclocondensation reaction under laser irradiation (1450 nm) [241]. Near-infrared LSPR of  $Cu_7S_4$  NPs core was responsible for the improved photocatalytic activity.

## 5.3. MNPs loading

The design of MNPs loading on ZIF-8 as photocatalysts is based on three points: (1) ZIF-8 provides a large specific surface area and would efficiently adsorb reactants [217–219,242,243]; (2) ZIF-8 as shell could play a “molecular sieve” role for reactants with specific sizes and stabilize the MNPs core for excellent recyclability [242,243], and (3) The photocatalytic activity mainly depends on the LSPR effect of MNPs due to the none photocatalytic activity of ZIF-8, especially under visible-light irradiation [217–219,242,243]. The LSPR effect enhances the activity of photocatalysts by extending light absorption to longer wavelengths and transferring the plasmonic electrons from the SPR metal to the CB of semiconductor [244].

Ag/AgCl NPs can harvest solar energy in a very broad visible spectra region due to the LSPR effect of Ag NPs. However, the photocatalytic

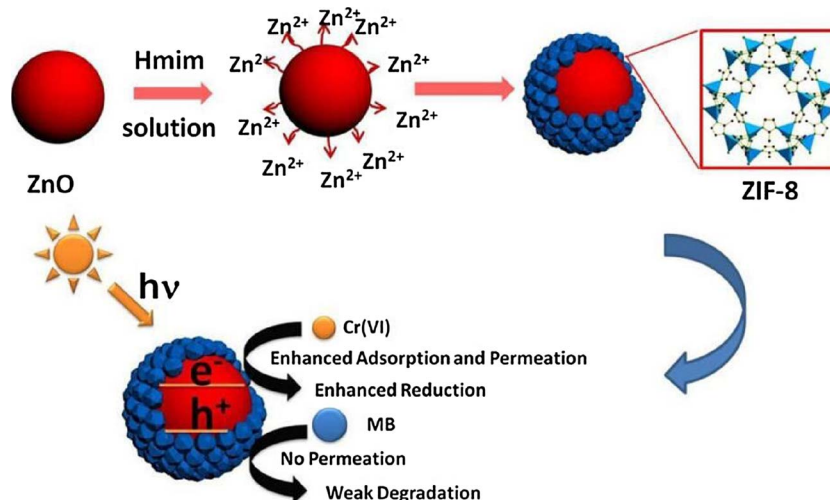


Fig. 23. The construction of  $ZnO$ @ZIF-8 and its selective photocatalytic reduction of  $Cr(VI)$  [236].



Fig. 24. The constructed process of  $\text{TiO}_2/\text{ZIF-8}$  nanofibers (NFs) [215].

activity of Ag/AgCl under visible-light irradiation is limited by its poor adsorption capacity and relatively weak reducing capacity [219]. Thus, loading them on ZIF-8 is a feasible way to address these problems [217–219]. Ag/AgCl@ZIF-8 was firstly fabricated by depositing the Ag/AgCl on the surface of ZIF-8 [217]. The photo-induced electrons could transfer from Ag/AgCl to ZIF-8 though the CB position of ZIF-8 ( $-0.86$  eV vs NHE) is very low. The prepared Ag/AgCl@ZIF-8 showed enhanced photocatalytic activity for the RhB degradation under visible-light irradiation. Liu and co-workers also synthesized Ag/AgCl/ZIF-8 for the photocatalytic degradation of RhB and the mechanism has been investigated thoroughly [219]. Meanwhile, they constructed Ag@AgCl/Ag nanofilm/ZIF-8 composites by loading Ag@AgCl and Ag nanofilm on the surface of ZIF-8 simultaneously via a deposition-photoreduction method [219]. The extended contact interface between Ag nanofilm and ZIF-8 promoted the quick electrons transfer and electron-hole pairs separation, leading to a remarkable improvement of photocatalytic activity for the degradation of MB. The encapsulation MNPs into the cavity of ZIF-8 is a typical design and has the merits of molecular sieving effect and high stability of metal nanoparticles. Chen and co-workers utilized PVP-Au NPS as nucleation seeds for ZIF-8 to selectively synthesize Au@ZIF-8 single- or multi-core-shell structures by epitaxial growth or coalescence of nuclei (Fig. 25a) [243]. The photocatalytic performance was evaluated by the oxidation of benzyl alcohol and the low conversion over Au@ZIF-8 compared to Au-SiO<sub>2</sub> was ascribed to the size-selectivity of ZIF-8. Recently, a core-shell Pd nanocubes (NCs) @ZIF-8 was utilized for the selective photocatalysis of the small olefins hydrogenation (Fig. 25b) [242]. The catalytic activity under  $100 \text{ mW cm}^{-2}$  visible-light irradiation at ambient temperature was the same as that of thermally driven (no light) catalytic hydrogenation at  $50^\circ\text{C}$ .

#### 5.4. Sensitization

Although ZIF-67 possesses a small band gap ( $E_g = 1.98$  eV), the efficiency for visible-light-driven photocatalysis of ZIF-67 is low when using single-component ZIF-67 due to the limited absorption in the solar spectrum. Its relatively small extinction coefficients of  $\text{Co}^{2+}$  d-d transitions ( $\sim 100\text{--}1000 \text{ mol L}^{-1} \text{ cm}^{-1}$ ) cause for this defect [245]. Expanding the absorption spectrum of ZIF-67 through sensitization by a chromophore is a desirable strategy that is similar to dye sensitization. Qin and co-workers synthesized ZIF-67 as a co-catalyst for photochemical  $\text{CO}_2$  reduction under visible-light irradiation by cooperation of dye photosensitizer  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (bpy = 2,2'-bipyridine), using triethanolamine (TEOA) as electron donor [246]. The  $\text{CO}$  generation rate reached to  $74.8 \mu\text{mol h}^{-1}$ , which was much higher than that of other types of MOFs (ZIF-8, UiO-66-NH<sub>2</sub> and MIL-101-NH<sub>2</sub>) (Table 5). A porous hybrid system by sensitizing the  $\text{RuN}_3$

photosensitizer on the surface of ZIF-67 for  $\text{H}_2$  production from water has been reported by Yang and co-workers [245]. According to the transient absorption spectroscopy, the energy transferred efficiency from the excited  $\text{RuN}_3$  to ZIF-67 reached to  $\sim 86.9\%$ , leading to the enhanced photocatalytic activity.

#### 5.5. Pyrolyzation

ZnO is a technologically important II-VI semiconductor with a wide direct band gap of  $3.37$  eV and a large excitation binding energy of approximately  $60$  mV [247]. Besides, ZnO has a higher electron mobility of  $115\text{--}155 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  compared to that of  $\text{TiO}_2$  (only  $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the most used  $\text{TiO}_2$ ) [248], suggesting ZnO particles or clusters may serve as the good electron trappers and transmission medium. Similar with  $\text{TiO}_2$  derived from MIL-125, the pyrolysis of ZIF-8 to ZnO with porous structure for photocatalysis also plays an important role and the studies were more than that of MIL-125. The pyrolysis of ZIF-8 had two strategies: one-step pyrolysis and two-step pyrolysis. The prepared ZnO were almost C/N doped, due to C and N doping could generally render electrons lighter and holes heavier, resulting in more visible-light harvesting and decreased recombination rate of photo-induced electron-hole pairs [249].

One-step pyrolysis of ZIF-8 is rapid and simple. The C-ZIF/g-C<sub>3</sub>N<sub>4</sub> composite was constructed via thermal condensation of ZIF-8 and melamine at  $650^\circ\text{C}$  under  $\text{N}_2$  flow [250]. The C-ZIF/g-C<sub>3</sub>N<sub>4</sub> composite with  $1 \text{ wt}\%$  C-ZIF onto g-C<sub>3</sub>N<sub>4</sub> showed highest photocatalytic activity for the  $\text{H}_2$  production under visible-light irradiation, which was  $36.2$  times higher than that of pure g-C<sub>3</sub>N<sub>4</sub> and  $2.8$  times higher than that of Pt/g-C<sub>3</sub>N<sub>4</sub>. The C-ZIF derived from the pyrolysis of ZIF-8 acted as a bifunctional electron acceptor and  $\text{H}_2$  production reaction cocatalyst in the photocatalytic  $\text{H}_2$  production. Mesoporous ZnO with the bimodal carbon modification (carbon doping and surface carbon coating) was prepared simultaneous during the pyrolysis of ZIF-8 in air [251]. The sample calcined at  $500^\circ\text{C}$  showed the highest photocatalytic  $\text{CO}_2$  reduction activity ( $0.83 \mu\text{mol h}^{-1} \text{ g}^{-1}$ ), which was about six folds higher than that of ZnO nanorods synthesized by a hydrothermal method. Porous N-doped ZnO through direct calcination of ZIF-8 and urea mixture was also prepared at  $550^\circ\text{C}$  [231]. The photocatalytic activity for RhB degradation was  $2.58$  times higher than that of ZIF-8-derived ZnO under visible-light irradiation. To accurately investigate the contents and types of nitrogen in the calcined ZIF-8, Zhao and co-workers prepared N-doped graphene analogs by calcining ZIF-8 under Ar atmosphere at different temperatures [252]. After the pyrolysis of ZIF-8, the N-doped graphene analogs not only retained the polyhedron structure but also possessed nitrogen contents of  $9\text{--}15 \text{ wt}\%$  depending on the calcination temperature. In addition, the total and relative contents of graphitic nitrogen, pyridinic nitrogen and pyrrolic nitrogen



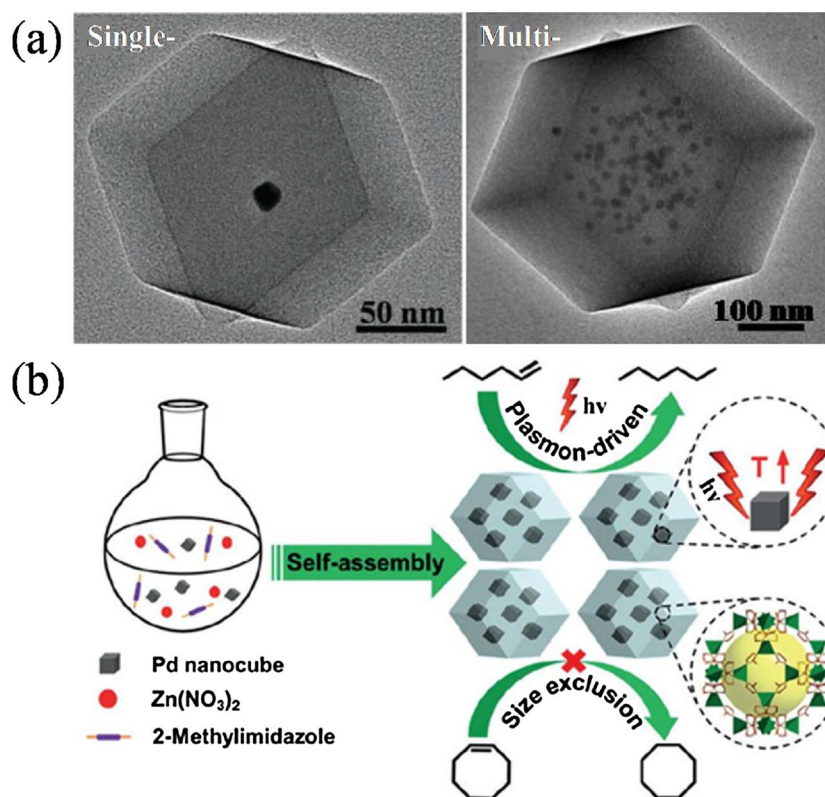


Fig. 25. TEM images of Au@ZIF-8 single- or multi-core-shell structures [243] (a) and self-assembly of Pd NCs@ZIF-8 and plasmon-driven selective catalysis of the hydrogenation of olefins [242] (b).

**Table 5**  
Photocatalytic CO<sub>2</sub> reduction performance promoted with various MOFs [246].

| MOFs                       | CO (μmol) | H <sub>2</sub> (μmol) | CO + H <sub>2</sub> (μmol) | Sel.CO (%) |
|----------------------------|-----------|-----------------------|----------------------------|------------|
| Co-ZIF-67                  | 29.6      | 14.8                  | 44.4                       | 66.7       |
| Zn-ZIF-8                   | 1.8       | 2.0                   | 3.8                        | 47.4       |
| Cu-MOF                     | 1.2       | 1.5                   | 2.7                        | 44.4       |
| Zr-Uio-66-NH <sub>2</sub>  | 0.9       | 1.2                   | 2.1                        | 42.9       |
| Fe-MIL-101-NH <sub>2</sub> | 4.7       | 2.1                   | 6.8                        | 69.1       |

in the N-doped graphene analogs could also be well-tuned through the calcination. The N-doped graphene analogs derived from ZIF-8 calcined at 1000 °C exhibited the highest photocatalytic activity for H<sub>2</sub> production from water splitting due to the existence of the highest content of graphitic nitrogen. In 2017, an extraordinary ZnO@C-N-Co core-shell

nanocomposite was constructed by directly pyrolyzing a hollow Zn/Co-ZIF matrix consisting of a ZIF-8 shell with some Co-ZIF nanoplates inside the hollow cavity at 600 °C under an argon atmosphere [253]. Interestingly, the ZIF-8-shell-derived ZnO NPs could agglomerate spontaneously and move to the hollow cavity while the internal Co NPs transferred inversely to the linker-derived N-C shell during the pyrolysis process (Fig. 26). The unique composites showed a remarkable photocatalytic activity and excellent recyclability for the degradation of MO. Meanwhile, Pt-ZnO-Co<sub>3</sub>O<sub>4</sub> was also constructed by pyrolysis of bimetallic ZnCo-ZIFs followed by doping Pt NPs [254]. Compared to the ZIF-8 and ZIF-67-based derivatives, Pt-ZnO-Co<sub>3</sub>O<sub>4</sub> had a higher photocatalytic hydrogen generation rate.

Recently, two-step pyrolysis of ZIF-8 to produce ZnO for photocatalysis was also investigated. Compared with ZnO prepared via one-step pyrolysis, two-step pyrolytic ZnO possesses lots of merits, including

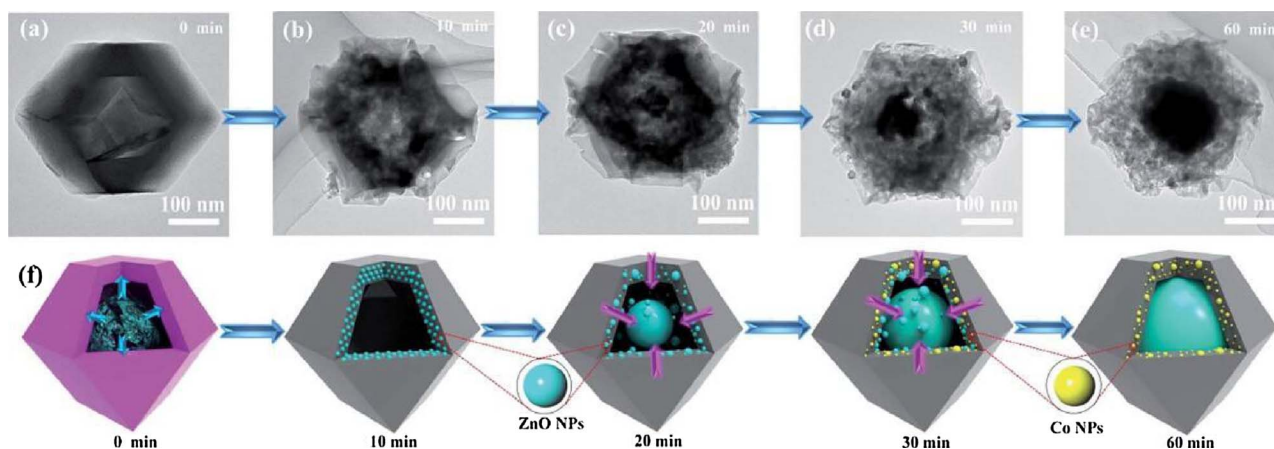


Fig. 26. TEM images of the products collected at different pyrolysis times (a–e) and Schematic illustration of the formation process of the core-shell ZnO@C-N-Co (f) [253].

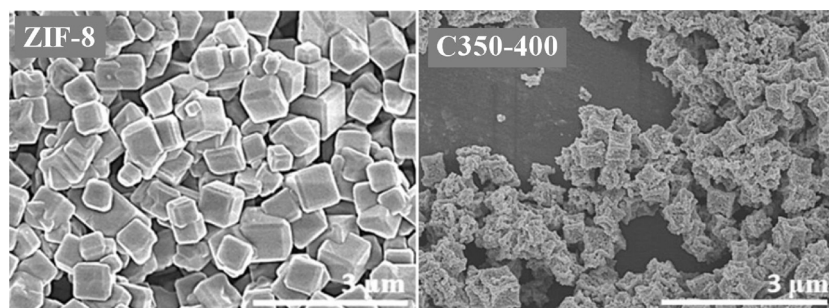


Fig. 27. SEM images of pristine ZIF-8 and C350-400 sample [255].

the higher surface area, more amounts of C doping and higher optical absorption. More importantly, the two-step calcined samples showed much higher photocatalytic activity than that of one-step calcined samples [255–257]. In 2016, Pan and co-workers prepared C-doped ZnO by two-step calcination of ZIF-8 (SEM images are shown in Fig. 27) and the sample C350-400 (C-doped ZnO, firstly calcined at 350 °C for 2 h, then 400 °C for 1 h) showed an increased photoactivity that was about three-fold and four-fold higher than ZnO (C450) in photocatalytic degradation of RhB and photoelectrochemical (PEC) water splitting under UV–vis irradiation [255]. Liang and co-workers also synthesized C, N-doped ZnO by two-step pyrolysis of ZIF-8 [256,257]. Firstly, ZIF-8 carbonization in a nitrogen atmosphere limited Zn into porous carbon, and the followed calcination in air formed nanosized ZnO photocatalysts. The hybrids were evaluated by photocatalytic degradation of MB and oxygen evolution reaction (OER). However, the two-step pyrolysis is more complex than one-step pyrolysis relatively.

#### 5.6. Incorporation with other functional materials

A hybrid composite ZIF-8/black phosphorus (BP) was composed of ZIF-8 NPs uniformly distributed on the surface of BP nanosheets [258]. BP functionalized with polyvinylpyrrolidone (PVP) was promoted for the in situ growth of ZIF-8, and the pyrrolidone rings (C=O) enhanced the affinity between Zn ions and BP. The obtained nanocomposites exhibited excellent catalytic efficiency on photocatalytic degradation of MB. Activation of peroxymonosulfate (PMS) represents a widely-used chemical oxidation reaction for chemical synthesis and environmental remediation. Lin and co-workers used ZIF-67 to activate PMS and the degradation activity of RhB was enhanced under UV-light irradiation [259].

Although the large band gap energy and low CB potential of ZIF-8 limited its applications in photocatalysis, the regular topological structure, rapid synthesis and easy to control of ZIF-8 still attract huge attention in photocatalytic fields. The modified strategies of ZIFs and their corresponding applications are listed in Table 6.

#### 6. Other MOFs

Most of studies focused on the modification to above-mentioned three types MOFs (UiOs, MILs and ZIFs). A primary reason is that their good stability. The above MOF-based photocatalysts could retain crystallinity and activity at least three recycles in water, weak acid and base according to the previous reports [36,37,70,260,261]. Except the major three types of MOFs, there are still a small number of other stable MOFs modified for photocatalysis, e.g. HKUST-1 [262–267], NTU-9 [268].

HKUST-1 is composed of 1, 3, 5-benzenetricarboxylate linkers coordinating with copper ions in a cubic lattice. It possesses a relatively large band gap that is more than 3 eV [266,267]. In 2014, Abedi and co-workers prepared a stable mesoporous HKUST-1 via a surfactant-assisted templating method [262]. After a suitable amount of amorphous titania (70 wt%) incorporated into the meso-HKUST-1, the conversion of sunlight-driven selective aerobic photooxidation could reach 100%

and the corresponding selectivity was 99%. Mosleh's research group has done lots of work based on HKUST-1 for photocatalysis. They prepared BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub>-HKUST-1 composites and applied it in a catalytic rotating packed bed reactor [264]. The toluidine blue and auramine-O in the reactor could be simultaneous photocatalytic degradation under visible-light illumination. Later, they synthesized Ag<sub>3</sub>PO<sub>4</sub>/AgBr/Ag-HKUST-1 to instead of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub>-HKUST-1 as photocatalysts and realized the simultaneous degradation of ternary mixture (MB, auramine-O and erythrosine) [265]. The research group of Majid also prepared Ag<sub>2</sub>CrO<sub>4</sub>/HKUST-1 [266] and Ag/Ag<sub>3</sub>PO<sub>4</sub>/HKUST-1 [267] composites for the photocatalytic degradation of azo dyes Congo Red and Ponceau BS. Pyrolyzation had been used in HKUST-1 as well. Zhang and co-workers developed magnetic Fe<sub>3</sub>O<sub>4</sub>@C/Cu and Fe<sub>3</sub>O<sub>4</sub>@CuO nanocomposites with a core/shell structure via direct calcinations of Fe<sub>3</sub>O<sub>4</sub>@HKUST-1 in N<sub>2</sub> and air respectively [263]. Results demonstrated that the Fe<sub>3</sub>O<sub>4</sub>@C/Cu performed obvious activity in the degradation of MB under visible-light illumination in the presence of H<sub>2</sub>O<sub>2</sub> compared with Fe<sub>3</sub>O<sub>4</sub>@CuO nanocomposites, TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. After the first synthesis of NTU-9, Kaur and co-workers firstly modified NTU-9 by mixing CdTe quantum dots in its formation liquid. The prepared composites showed enhanced activity for the visible-light driven photocatalytic degradation of rhodamine 6G.

#### 7. Conclusions and outlook

Various MOFs have emerged as photocatalysts, where pristine MOFs were introduced from UV-light response to visible-light response, and MOFs modifications were developed in the following aspects: decoration of organic linker or metal center, combination with semiconductors, MNPs loading, decoration with RGO, sensitization, pyrolyzation and incorporation with other functional materials. Although intense work has been carried out to investigate MOFs for photocatalysis, mainly concentrating on UiO-66(Zr), MIL-125(Ti) and ZIF-8(Zn), because they are robust enough to survive harsh catalytic conditions and possess perfect crystal structures. However, these MOFs lack redox-activities and visible-light response, which limited their applications and photocatalytic efficiency under visible-light irradiations. The photocatalytic applications mainly focused on H<sub>2</sub> production, CO<sub>2</sub> reduction and environmental remediation. Few MOFs were used for photocatalytic organic synthesis. In addition, MOFs are normally synthesized by a solvothermal method with raw materials that are expensive compared to conventional photocatalysts (e.g. TiO<sub>2</sub>) and the stability is still a problem. Hence, MOFs as photocatalysts for practical applications are promising but remain a great challenge.

To combat these aforementioned problems, several approaches could be attempted: 1) as metals like Fe and Co have the redox-activities and visible-light response, the research hotspots will likely transfer to visible-light responsive MILs (MIL-101(Co), MIL-100(Fe) and MIL-53(Fe)) for photocatalysis. 2) More modified MOFs as photocatalysts should be tried to use in organic synthesis reactions, such as oxidation of alcohol, Suzuki reaction and even hydrogenative cyclization. 3) Improving synthetic efficiency for existing MOFs and developing new

**Table 6**  
Modified strategies of ZIFs and their corresponding applications.

| Strategies                           | Details   | MOF  | Applications                            | Light source | Ref.      |
|--------------------------------------|---|--|---|--------------|-----------|
| Partial substitution of metal center | Cu  | ZIF-67   | MO degradation                          | Visible      | [233]     |
|                                      | Ni  | ZIF-8  | MB degradation                          | Visible      | [234]     |
| Combination with semiconductors      | ZnO   | ZIF-8  | Cr(VI) reduction                        | UV           | [236]     |
|                                      | ZnO   | ZIF-8  | MB degradation                          | UV           | [235]     |
|                                      | ZnO   | K <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> /ZIF-8 | MB, RhB degradation                     | UV-vis       | [237]     |
|                                      | Zn <sub>2</sub> GeO <sub>4</sub>                          | ZIF-8  | CO <sub>2</sub> reduction               | UV-vis       | [232]     |
|                                      | g-C <sub>3</sub> N <sub>4</sub>                           | ZIF-8  | CO <sub>2</sub> reduction               | UV-vis       | [239]     |
|                                      | g-C <sub>3</sub> N <sub>4</sub>                           | ZIF-8  | Tetracycline degradation                | Sunlight     | [240]     |
|                                      | TiO <sub>2</sub>  | ZIF-8  | RhB degradation                         | UV           | [215]     |
|                                      | TiO <sub>2</sub>  | ZIF-8  | Cr(VI) reduction                        | UV-vis       | [238]     |
|                                      | Cu <sub>7</sub> S <sub>4</sub>                            | ZIF-8  | Cyclocondensation                       | Laser        | [241]     |
|                                      | Cd <sub>0.5</sub> Zn <sub>0.5</sub> S                     | ZIF-8  | Cr(VI) reduction                        | Visible      | [111]     |
| MNPs loading                         | Ag  | AgCl/ZIF-8   | RhB, MB degradation                     | Visible      | [217–219] |
|                                      | Au  | ZIF-8  | Alcohols oxidation                      | Visible      | [243]     |
|                                      | Pd  | ZIF-8  | Olefins hydrogenation                   | UV-vis       | [242]     |
| Sensitization                        | [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O | ZIF-67   | CO <sub>2</sub> reduction               | Visible      | [246]     |
|                                      | RuN <sub>3</sub>  | ZIF-67   | H <sub>2</sub> production               | Visible      | [245]     |
| Pyrolyzation                         | ZnO   | ZIF-8  | CO <sub>2</sub> reduction               | UV-vis       | [251]     |
|                                      | (C-ZIF)/g-C <sub>3</sub> N <sub>4</sub>                   | Melamine/ZIF-8   | H <sub>2</sub> production               | Visible      | [250]     |
|                                      | C,N doped ZnO   | ZIF-8  | MB degradation, oxygen evolution        | Visible      | [256]     |
|                                      | ZnO@C-N-Co  | Zn/Co-ZIF  | MO degradation                          | UV-vis       | [253]     |
|                                      | N-doped ZnO   | Urea/ZIF-8   | RhB degradation                         | Visible      | [231]     |
|                                      | N-doped ZNG   | ZIF-8  | H <sub>2</sub> production               | UV-vis       | [252]     |
|                                      | C-doped ZnO   | ZIF-8  | RhB degradation and PEC water splitting | UV-vis       | [255]     |
|                                      | C-N-ZnO   | ZIF-8  | MB degradation and OER                  | UV-vis       | [257]     |
|                                      | Pt-ZnO-Co <sub>3</sub> O <sub>4</sub>                     | Zn/Co-ZIF  | H <sub>2</sub> production               | UV-vis       | [254]     |

MOFs that contain redox active metals (e.g., Co, Ni, Mn, Fe) and/or functional organic linkers (e.g., imidazolate, porphyrin, pyridine) are worthy of study. 4) Adding some template agent in the corresponding synthesis solutions is a desirable way to further improve the crystallinity and stability of MOFs [28]. It is noticed that constructing multi-functional MOF photocatalysts is an interesting but tough work, which means that the oxidation reaction and the reduction reaction occur simultaneously on both sides. Up to now, Cr(VI) reduction and dyes oxidation have been realized in one system [62,95,209]. Multi-functional MOF photocatalysts are required in the more advanced reactions in one system, such as water splitting/CO<sub>2</sub> reduction. All in all, MOF-mediated photocatalysts currently are still in their infancy and hold a great potential in energy regeneration and environmental remediation in the future. We anticipate that this review will provide an essential resource for guiding both academic and industrial research to design or select the most appropriate photocatalytic materials.

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